STUDIES ON

THE THERMODYNAMICS OF ION ASSOCIATION

IN AQUEOUS SOLUTION

A Thesis

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BY

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FORWARD.

The work described in this thesis was carried out in the Physical Chemistry Department of the Institute of Chemistry at the University of Glasgow, which is under the direction of Professor J.M. Robertson, F.R.S.

I am indebted to Dr. George H. Mancollas, under whose supervision this work was performed, for his encouragement and guidance throughout my research degree course and, to Dr. Helen S. Dunsmore who wrote all the computer programmes. Thanks are due to the Staff of the Glassblowing and Engineering Workshops for the construction of the calorimeters.

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SUMMARY.

Three sensitive calorimeters have been used to measure the heats of formation of complexes in aqueous solution. With a knowledge of the accompanying free energy changes, the corresponding entropies of association have been calculated. A knowledge of entropy and enthalpy changes provides a clearer insight into the nature of the chemical processes than does the free energy changes alone.

The thesis is divided into three parts. A general introduction proceeds Part I which describes the development and calibration of the calorimeters and the use of one of them in measuring the heats of formation of complexes of some divalent transition metal ions with the glycinate anion.

A calorimetric investigation of the heats of formation of divalent alkaline earth and some other metal ions with di-(2-aminoethoxy)- ethanetetraacetic acid, (EGTA), and diaminoethane N,N' di-(o-hydroxyphenylacetic acid), (EHPG), is described in Part II. No values for the heats of protonation of EHPG have been reported and these have been determined calorimetrically. The thermodynamic data are

compared with those of similar complexes with other polyaminocarboxylate and polycarboxylate ligands.

Attempts to measure calorimetrically the heats of hydrolysis of the thallic ion, Tl(III), are described in Part III.

All investigations were carried out at a constant ionic strength of 0.1 M, and data were processed on an English Electric KDF9 computer.

GENERAL INTRODUCTION

GENERAL INTRODUCTION:

The interaction between a hydrated metal ion and an anion or neutral ligand in aqueous solution may be represented by,

$$M^{n+}_{aq} + A^{m-}_{aq} \rightleftharpoons (M^{n+}_{aq} , A^{m-}_{aq}) \rightleftharpoons (M^{n+} H_2O A^{m-})_{aq} + xH_2O$$

$$\rightleftharpoons (MA^{(n-m)+})_{aq} + (x+1)H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

in which a number of solvated and partially solvated species participate in a series of equilibria. By application of the Law of Mass Action to the formation of a 1:1 species, a thermodynamic association constant may be defined by,

$$K = \{MA^{(n-m)+}\} / \{M^{n+}\}\{A^{m-}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

in which the braces enclose activities. The free energy change, ΔG, for the association is then given by,

$$\Delta G = -RT \ln K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

It can be seen in (1) that the association between ions in solution need not result in identical ion pairs being formed, and a formal distinction can be made between outer -

and inner - sphere species. In the former, one or at most two, solvent molecules are interposed between the interacting ions whilst in the latter, the ions are adjacent to one another. In the determination of association constants most methods used are incapable of distinguishing between these alternatives and it is important to recognise that different methods may respond to different types of species. Whereas conductance and electromotive force measurements will detect distant ion pairs, spectrophotometric measurements, especially in the visible spectrum, will be expected to detect only those ion pairs with the associating ions in close proximity. Changes in the ultra - violet however, may also reflect the presence of species formed in less close interactions and so, in principle, the method is capable of distinguishing between outer - and inner-sphere ion pairs. For transition metals it has been suggested [1] that outer - sphere ion-pair formation will be expected to have very little effect on the low - intensity absorption bands in the visible spectrum. These are due to forbidden d - d transitions, the wavelength depending upon the separation of the d - d states which, in turn, is a function of the polarisation of the cation by the associating ligand. Outer - sphere interaction will have only a very small influence on the d - d splitting because of the large separation of the ions.

With spectrophotometric measurements it has been possible to conclude, on this basis, that the interactions in cobaltous sulphate and thiosulphate are outer - and inner - sphere respectively, even though their thermodynamic association constants are about equal [2]. Information on the relative amounts of inner - and outer - sphere species in the association of a number of ions has also been obtained using similar visible and ultra - violet spectroscopic approaches.

Some workers have replaced the terms outer - sphere and inner - sphere with "ion - pair " and " complex " respectively to distinguish between the two types of species. A better description, however, of ionic interactions is obtained if the terms outer - and inner - sphere are used to describe the type of association in question and an "ion - pair" is regarded as a species in which the bonding is almost entirely due to long - range electrostatic forces between the oppositely charged ions. Attaching this wider meaning to the term "ion - pair", solvent molecules may or may not be interposed between the ions. In complexes, on the other hand, there will be a contribution to the stability by short-range or covalent forces, and this will certainly involve inner-sphere interaction with the elimination of one or more solvent molecules from the co - spheres of the ions.

The existence of inner - and outer-sphere associations is very clearly demonstrated in the ultrasonic absorption spectra of certain electrolyte solutions. If a reaction is subjected to a periodic pressure disturbance, as in an ultrasonic wave, absorption maxima may be obtained at certain frequencies when the periodic time is comparable with the relaxation time of the reaction. The absorption curves for the bivalent metal sulphates showed two distinct maxima which could be attributed to specific interactions between the ions after they had approached close enough by diffusion (process I below) in the reaction scheme [3]:

$$M^{2+}_{aq} + SO_4^{2-}{}_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[M^{2+}(H_2O)_2SO_4^{2-}\right]_{aq} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \left[M^{2+}(H_2O)SO_4^{2-}\right]_{aq} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \left[M^{2+}SO_4^{2-}\right]_{aq}$$

(1) (2) (3)

The higher - frequency maximum, having a frequency almost independent of the nature of the cation, could be attributed to process (2) where the ions remain separated by solvent molecules. The lower - frequency maximum was sensitive to the nature of the cation and corresponded to process (3) where the last intervening solvent molecule is expelled.

The ratio k_3/k_{-3} was found to be approximately 0.1 for all cations which indicated that only about 1e% of the ion - pairs were of the inner - sphere type.

The equilibrium between outer - and inner - sphere species in solution is usually rapidly established but Fogel, Tai and Yarborough were able to separate the inner - and outer - sphere chromium (111) monosulphate complexes on an ion - exchange column.[4] The trivalent metal ion and the outer - sphere ion pairs in equilibrium with it are held preferentially by the cation exchanger and the singly charged inner - sphere species are allowed to pass through. The authors deduced the equilibrium constants,

$$K(\ CrSO_4^{+}\ _{aq}) = 33 \quad \text{and} \quad K(\ Cr^{3+}(H_2O)SO_4^{2-}\ _{aq}) = 12,$$

which imply that the ratio of the concentrations of inner - to outer - sphere species is about 3:1 at equilibrium. As is to be expected, this is much higher than the corresponding ratio, 1 : 10, for the bivalent metal sulphates.

In some cases it is possible to determine experimentally whether ion - pairs or complexes are being formed. The measurement of Raman spectra affords a powerful method for detecting specific interactions but suffers from the disadvantage of being restricted to rather concentrated solutions, when most interest is in the species present in dilute solutions. Bjerrum , from purely electrostatic considerations,

defined a distance between oppositely charged ions within which they are to be considered as being associated into ion - pairs [5]. This distance, q, the ionic separation at which the mutual potential energy is equal to the thermal energy, kT, represents the position of minimum probability of finding an ion of opposite charge anywhere on a spherical shell of radius q surrounding the central ion, and is given by,

$$q = z_+ z_- e^2/2\epsilon kT ,$$

where Z_+ and Z_- are the charges on the ions, ϵ is the dielectric constant of the solution and k is the Boltzmann constant. The association constant for an ion pair can be written,

$$K = \frac{4\pi N}{1000} \int_a^q \exp\left[\frac{u(r)}{kT}\right] r^2 \, dr,$$

where r is the distance between the centres of the two ions. Introducing the value, $u(r) = -z_+ z_- e^2/\epsilon r$, for the electrostatic work required to bring an anion from infinity to a distance r from a cation, gave the classical Bjerrum equation,

$$K = \frac{4\pi N}{1000} \int_a^q \exp\left[\frac{-z_+ z_- e^2}{\epsilon kT}\right] r^2 \, dr \quad \ldots\ldots\ldots\ldots (4)$$

In this treatment two oppositely charged ions between a, the distance of minimum approach and q, the minimum value of

the integral in equation (4) are considered to form an ion - pair. By substituting $K = 5.5 \times 10^{3}$ l. mole^{-1} for lanthanum ferricyanide into equation (4), the closest distance of approach is 7.2 Å [6]. In contrast to this, impossibly small distances are calculated for $PbCl^{+}$ and $CdCl^{+}$ (which are simply first stages in the formation of higher halide complexes), and for thallous ion - pairs, and this has been used as evidence for covalent bond formation. Bjerrum's theory, however, predicts ion - pairing for a large class of 2:1 electrolytes, such as the alkaline earth halides, but ion - pairs cannot be detected experimentally in these solutions and Davies has suggested that definite classification into ion - pairs and complexes on this basis should not be made [7].

For a series of reactions in which the ligand is kept constant the dependence of the overall free energy changes on the standard free energies, $G^{\circ}[M^{n+}]_{aq}$ of the metal ions is indicative of complex formation, whereas for ion - pairs, when the two ions interact without disturbing their hydration sheaths, the energy will depend on the ionic charges and the distance between them, and this distance, being a function of the hydration radius, will not vary appreciably [8].

Since experimentally determined association constants can vary over a very wide range of values, some attempts have been made to classify the metal ions in terms of their complexing ability. To consider them to be rigid, non - polarisable particles is to over simplify the problem and in practice, the deformability of the metal ion and the way in which the electronic structure is modified by interaction with the ligand must be taken into account. Schwarzenbach proposed that the metal ions be divided up into three classes [9]. Class A included the cations with a noble gas configuration, such as the alkali and alkaline earth metals, for which purely electrostatic bonding predominates. In this group, the association constants will be expected to increase with decreasing cationic size and increasing charge. Fluorine and oxygen donor atoms are most strongly bound by these cations and water is more strongly bound than ammonia on account of its greater dipole moment. These cations have little tendency to form complexes with cyanide ion since the latter exists under alkaline conditions which favour the formation of hydroxyl complexes. Class B included metal cations with completely filled d subshells, such as Cu^{+} , Ag^{+} , Zn^{2+} and Cd^{2+} , which undergo predominately covalent interactions, and the factors governing

ion - pair formation in Class A no longer hold. Instead of charge and radius, the difference in the electronegativities of the metal ion and the donor atom of the ligand becomes more important in influencing the extent of the complex formation. Thus the association constant increases with the ease with which the metal ion accepts and the donor atom donates electrons. Since electronegativities decrease in the order $F > O > N > Cl > Br > I \approx S$, the values of the association constants with a given group B metal ion follow the reverse order. Ammonia is more readily co-ordinated than water, and cyanide more than hydroxide. The transition metal ions with incomplete subshells constitute Class C, in which the characteristics of both classes A and B can be distinguished. The divalent metal ions Mn, Fe, Co, Ni and Cu have been most extensively investigated and in this series the ionic radius decreases and the ionisation potential increases up to copper. These factors satisfactorily account for the observed increase in association from manganese to copper and the sequence of stability,

$$Mn < Fe < Co < Ni < Cu > Zn,$$

forms the well known Irving - Williams series [10]. The sequence is particularly pronounced when the co-ordinating atom is nitrogen, carbon or sulphur rather than oxygen.

The latter members of the group, such as Cu(II), which have almost completely filled d subshells resemble class B metals, whereas Mn(II) and Fe(II) are more like class A metals.

The above classification serves as a useful guide as to the behaviour of metal ions but, in a more detailed discussion it is necessary to take into account other factors such as the possibility of π - bonding and the application of ligand - field theory.

Since the electrostatic fields set up by charges separated by distances on the atomic scale are of enormous intensity, it is necessary to take account of major perturbations of the electron charge cloud and of the electron energies. The basis for such a treatment was provided by the work of Bethe [11] and van Vleck [12]. If a complex is considered to be a symmetrical assembly of anions or dipoles around a central metal cation with the charges on the ligands, or the negative ends of their dipoles, directed towards the central atom, ligand - field theory [13] attempts to explain, for a given steric arrangement of the ligands, how the electronic system of the central metal atom is perturbed and how far this perturbation stabilises the postulated structure. The essential physical idea of the theory is that the electrons of the central

ion will tend to avoid those regions of space in which the field due to the attached negatively charged ions or dipoles is largest. In the case of an octahedral complex, the five d orbitals (d_{xy}, d_{xz}, d_{yz}, d_{z^2}, and $d_{x^2-y^2}$) of the metal cation, degenerate when the ion is uncomplexed, will be perturbed by interaction with ligands lying along the x- , y- and z axes. The electrostatic repulsion between these ligands and the electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals will be considerably greater than that with the electrons in the other three d orbitals. Hence the five-fold degeneracy of the d orbitals is split into a doublet, e_g, of higher energy and a triplet, t_{2g} , of lower energy. The energy separation between the two levels, designated Δ , can be determined from spectroscopic measurements and depends primarily upon the nature of the ligand and the charge on the cation. Since the energy rise of the two e_g orbitals must equal the energy drop of the three t_{2g} orbitals, the values $-0.4\ \Delta$ and $+0.6\ \Delta$ can be assigned to the t_{2g} and eg levels respectively.

The distribution of d electrons amongst the t_{2g} and e_g orbitals is of great importance, and complications arise when more than three d electrons are involved since there is a choice either of putting as many as possible into the lower energy t_{2g} orbitals or of distributing them so as to maintain the

maximum number of parallel spins. If the field set up by the ligands is strong, the energy of an electron in the e_g orbitals may be raised so much that the energy for a state in which all the electrons are paired up in the t_{2g} triplet may be lower than that of a state in which electrons are so distributed between the e_g and t_{2g} orbitals to give the maximum number unpaired, in accordance with Hund's rule. On this basis the same metal ion may exist in octahedral complexes with the electrons in the d orbitals distributed to give either the maximum number of parallel spins or the maximum amount of spin pairing, depending on the field strengths produced by the ligands. The ferric ion, Fe(III), which has five d electrons, illustrates this very clearly in its complexes with the cyanide ion, CN^-, and the flouride ion, F^-. The magnetic moment, μ, of the complex ion $Fe(CN)_6^{3-}$ is 2.35 whereas that of the ion FeF_6^{3-} is 5.92 which is indicative of there being five unpaired electrons in the latter and only one in the former, due to the greater field strength produced by the cyanide ion.

The terms inner - orbital, or low - spin, and outer - orbital, or high - spin, are applied respectively to the cyanide and the flouride complexes and in general to complexes of a similar type. Although the magnetic moments, which are a function of the number of unpaired electrons, for a series of complexes

of the same metal ion may change discontinuously at certain ligand - field strengths, this does not correspond to a discontinuous change in the nature of the central ion - ligand forces at any stage.

Ions with electronic configurations d^0 , d^5 and d^{10} will be essentially spherically symmetrical and the gas phase heats of formation of their complex ions, ΔH_g , will be expected to vary smoothly with atomic number [13]. In high spin complexes, the d^1, d^2, d^3, d^6, d^7 and d^8 electrons will occupy the lower t_{2g} orbitals and stability will be gained in excess of the smooth change from d^0 through d^5 to d^{10}. For the ions with d^4, d^5, d^9 , and d^{10}, electrons, the extra electrons are forced into the upper e_g level and the extra stabilisation is, at least, partly lost [14] . The orbital stabilisation may be expressed by

$$\text{Stabilisation} = (0.4n_{t_{2g}} - 0.6n_{e_g}) \Delta \quad \ldots\ldots\ldots\ldots (5)$$

where $n_{t_{2g}}$ and n_{e_g} are the numbers of electrons in the t_{2g} and e_g levels respectively. For low - spin and tetrahedral complexes, different arguments must be used but ΔH_g again has a node at the d^5 metal ion [13].

For complex reactions in which water molecules are displaced by ligand molecules, L , the additional ligand - field stabilisation for ions intermediate between d^0, d^5 and d^{10} may be calculated from an expression similar to (5) with $(\Delta_{H_2O} - \Delta_L)$,

the difference in energy separations induced by water and the other ligand, in place of Δ . Holmes and McClure studied the absorption spectra of crystalline hydrates of the transition metal ions and calculated the crystal - field stabilisations by the above method [15]. When these terms were subtracted from the hydration energies, the corrected values fell on the predicted smooth curve.

Ligand - field effects thus produce contributions to the heats of complex formation and in most cases the theory accounts satisfactorily for much of the observed ΔH data, while, at the same time, a number of anomalies created by the Irving - Williams treatment are also satisfactorily explained [14,16].

Until recent years the limited amount of heat data available has led many workers to consider only the free energy change, ΔG , when describing the type of ion association without considering the accompanying enthalpy, ΔH , and entropy, ΔS , contributions. The three functions are related by the expression,

$$\Delta G = \Delta H - T\Delta S, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

and, in order to gain an insight into the factors which affect the equilibrium, it is more useful to regard the free energy change as being a consequence of the changes in heat and entropy. The enthalpy change is the property most directly related to the changes in the numbers and strengths of bonds as the system

passes from reactants to products. The entropy change is a measure of the change of randomness, and the driving force in this process is the tendency for the system to go to the most probable, the most random, state. There are endothermic reactions which are made possible by favourable entropy changes, and there are exothermic reactions which do not take place because of unfavourable entropy changes. Any comparison of K values for a series of association reactions in which one ion is kept constant involves the assumption that variations either in ΔH or ΔS throughout the series may be neglected. It is clearly desirable to measure ΔH and this can be done either by studying the association constant over a range of temperatures or else by direct calorimetric methods.

The variation of log K with temperature can be described by an equation of the form,

$$\log K = a + bT + cT^2 + \ldots\ldots$$

The parameters a, b, and c can be obtained by substituting values of K at three temperatures and solving three simultaneous equations. Values of ΔH can then be calculated by differentiating log K with respect to temperature and while these values can be reliable if a large enough temperature range is covered, there are obvious advantages in measuring the heats of complex formation by a direct calorimetric method.

During the course of the present work, three different differential calorimeters were constructed and tested. In one, a thermocouple was incorporated as the sensing element while in

the other two, thermistors were used. The calorimeters are described in Part I of this thesis which also deals with the calorimetric determination of the heats of formation of the complexes formed between cobalt (II), copper (II) and zinc (II) with the glycinate anion. The results obtained are compared with those of the corresponding dicarboxylate complexes to evaluate the effect of replacing an oxygen by a nitrogen co-ordinating atom in a ligand.

Part II is devoted to the calorimetric determination of the heats of formation of the complexes of the alkaline earth ions Mg(II), Ca(II), Sr(II) and Ba(II) with the anion of di-(2-aminoethoxy)-ethanetetraacetic acid, (EGTA), and tiaminoethane N,N' di - (o-hydroxyphenylacetic acid), (EHPG). The complexes of the transition metal ions Cd(II) and Zn(II) with EGTA have also been studied. The great interest in the aminocarboxylate ions lies in their ability to form very stable complexes with a wide variety of metal ions due to their multidentate nature which enables cholates to be formed. This has resulted in their frequent use as analytical reagents for the determination of metal ions in solution. Much of the work, stimulated by the application of the ligand - field theory, has been done with the transition metal complexes, particularly with the EDTA molecule, whereas the alkaline earth cations have

received less attention. The results for the heats of formation of the EDTA complexes have been accepted for publication in the Journal of the Chemical Society.

Part III describes attempts to measure the heat of hydrolysis of the thallic ion, Tl(III).

All measurements in parts I and II were done at an ionic strength of 0.1M in order to compare with other data.

All activity coefficients in this work were calculated from the extended form of the Debye - Hückel equation [49] proposed by Davies [50],

PART I

The Heats of Formation of some Transition Metal Glycinate Complexes.

INTRODUCTION:

Many attempts to unravel the nature of the complexes formed between metal ions and amino acids, peptides and proteins are to be found. To study these systems a variety of methods have been employed, directed mainly towards the determination of equilibrium constants, although in the last few years more attention has been paid to calorimetric determinations of thermodynamic functions. Since many such complexes are found in animal and plant tissue as enzymes etc., their study is of fundamental importance in understanding natural processes. It has been shown, for instance, that the occurence of certain diseases is intimately related to the amounts of copper complexes present in certain systems, as in fruit trees [17].

Although there have been comparatively few enthalpy determinations for systems of this type, sensitive calorimeters have been designed, and have been in use for many years. Lange [18] studied heats of dilution with a system of twin adiabatic calorimeters, one of which was used as a constant temperature reference. Each calorimeter contained a section of a 1,500 junction thermopile, and one of the calorimeters described in the present work was of similar design.

Pitzer [19], who measured enthalpy values for the bisulphite ion, used a non-isothermal calorimeter, and modifications of this have been used by Staveley [20, 21, 22] and others [23] for studies with amine and ethylenediaminetetraacetate complexes.

Where the amounts of material available are extremely small, such as the transuranium elements, microcalorimeters have been used in the study of heats of solution. Westrum and Eyring [24] studied the dissolution of neptunium in hydrocholoric acid, using a resistance thermometer to measure temperature changes of approximately 2×10^{-5}° C. More recently there has been an increasing use of thermistors in calorimeters, and two such calorimeters are described in this part of the thesis.

The association of the amino acid, glycine, with metal ions is a system which has been extensively studied [25, 26]. Mellor and Maley [27] and Nancollas [28] have used potentiometric measurements at constant, and at varying ionic strengths, and thermodynamic constants have been obtained by Monk from pH measurements [29]. Davies [30], Keefer [31] and Monk [32,33] have also calculated thermodynamic functions from the results of stability measurements of sparingly soluble metal iodates. Christensen has measured the heats of formation of the copper glycinate complexes calorimetrically by a thermometric titration procedure [34].

The work described in this part of the thesis consists of the calorimetric determination of the heats of formation of the complexes formed between the divalent metal ions cobalt, copper and zinc and the glycinate anion. As was done by Monk [29,32] it was assumed that only two complexes MA^+ and MA_2 were formed with these ions, under the conditions of study.

EXPERIMENTAL

Preparation of Reagents:

Glycine : AnalaR glycine was used without further purification.

Potassium Hyrdoxide : A sample of a saturated solution of potassium hydroxide, prepared from washed AnalaR sticks and boiled - out distilled water, was diluted with carbon dioxide free distilled water in a nitrogen atmosphere. The solution was stored in a pyrex container connected, via an air-tight Quickfit joint, to an automatic burette suitably protected with soda - lime tubes. It was standardised by titrating against weighed samples of potassium hydrogen phthalate, and the results of duplicate experiments agreed to 0.1%.

Potassium Glycinate : Carbonate - Free potassium hydroxide was added to a weighed sample of glycine contained in a standard flask under an atmosphere of nitrogen. The solution was made up to the mark with boiled - out distilled water. A slight stoichiometric excess of potassium hydroxide was added to ensure that the glycine was completely converted to the A^- form.

COBALT CHLORIDE: Stock solutions were prepared from the AnalaR salt and were standardised either by gravimetric analysis of the chloride, as silver chloride [35] or by using an ion - exchange column. In the latter method, 10 ml. portions were passed through a column of Amberlite I.R. 120 resin, in the hydrogen form, and the colum washed with distilled water until free from acid. The eluted hydrochloric acid was estimated by titration with standard sodium hydroxide.

CUPRIC PERCHLORATE: AnalaR perchloric acid was added to an excess of cupric oxide in a pyrex flask and the solution was heated, at approximately 80°C, for twelve hours. The remaining oxide was then filtered off and the copper solution was analysed with potassium iodide and sodium thiosulphate [35] and by using an Amberlite I. R. 120 ion - exchange column. Both methods of analysis agreed to within 0.2%.

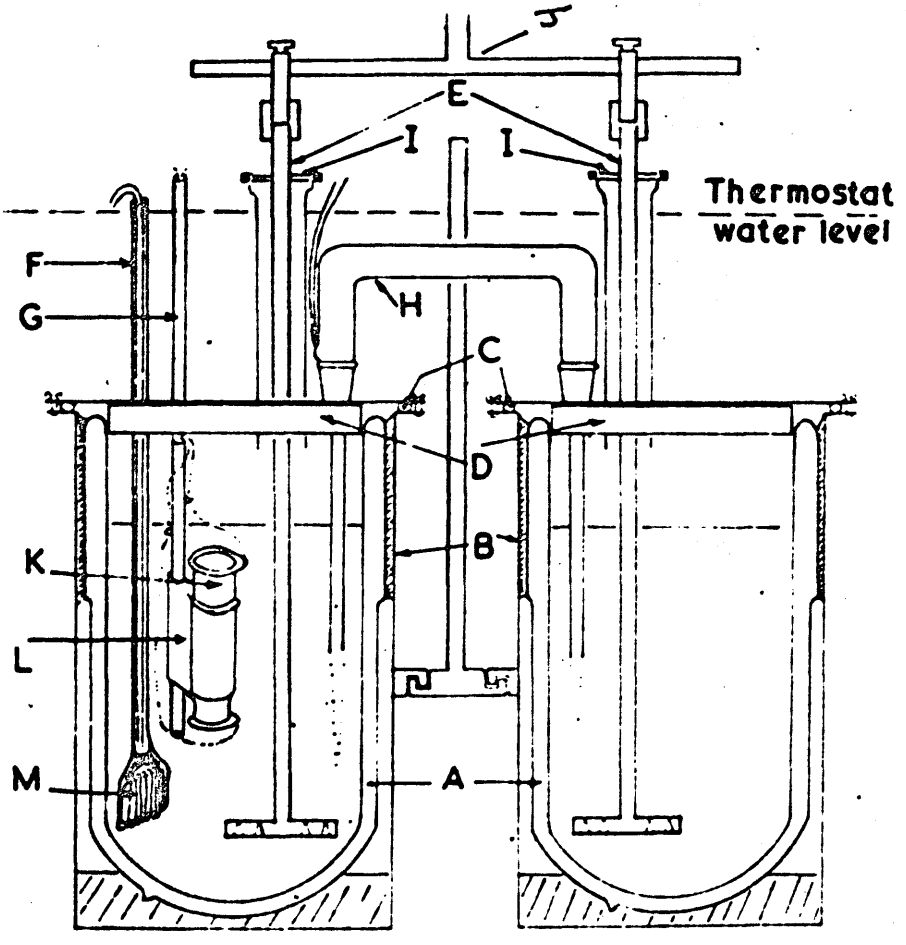
ZINC PERCHLORATE: Using zinc oxide, stock solutions were prepared in a similar manner to those of cupric perchlorate and analysed using an ion - exchange column.

Potassium chloride and potassium hydrogen phthalate were of AnalaR grade and were used without further purification.

All volumetric apparatus was of Grade A quality. Glassware was cleaned with ethanolic potassium hydroxide and chromic acid, and flasks were steamed for thirty minutes. Samples of reagents were weighed out from pyrex weighing bottles on an Oertling single-pan balance.

APPARATUS.

The differential thermocouple calorimeter is shown in Figure 1 . It consisted of two silvered Dewar flasks, of 1500 ml. capacity, cemented into brass containers. The rubber O-rings between the tops of these containers and the screwed down lids ensured a water-tight seal. Perspex discs of a half inch thickness, were cemented to the underside of the lids in order to reduce to a minimum the air space above the solutions in the Dewar vessels. Four holes in the lid of the first Dewar accommodated a nichrome wire heater, of known resistance, a vibro-stirrer diaphragm, a B 24 socket, for one end of a 60 junction copper -constantan thermopile, and a mixing device. Two holes in the lid of the second Dewar accommodated a vibro-stirrer diaphragm and a B 24 socket for the other thermocouple junction. In order to reduce to a minimum any heating effects caused by unequal stirring, both stirring rods were driven from the same vibrorotatory motor, (Vibro - Misher, Messrs. Shandon and Co. Ltd., England) by means of a specially designed chuck. The brass containers were bolted together and were completely immersed in a thermostat.



The calorimeter with fittings.

Fig. 1

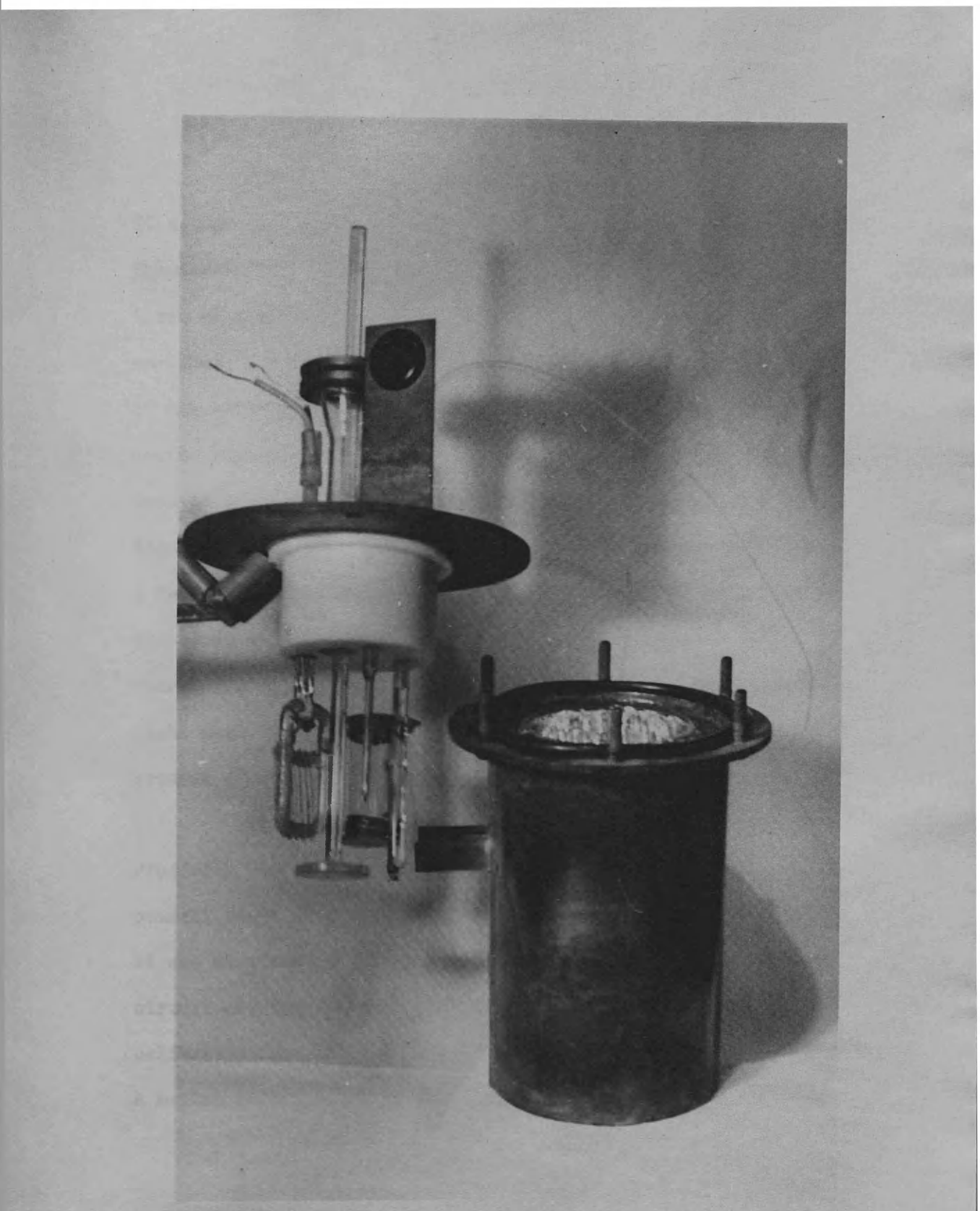


PLATE 1

The thermopile consisted of sixty junctions of 20 s.w.g. constantan wire and 34 s.w.g. enamelled copper wire. The constantan wires were insulated to within $\frac{1}{4}$ of an inch of their ends with P.V.C. sleeving and the copper wires were wound on these. The junctions were made by soft soldering the ends of the wires and were arranged to be at regular intervals of depths when placed in the Dewar vessels. Araldite cement was used to insulate the junctions and the thermocouple was securely bound with nylon thread. The wires were placed inside a rubber tube which had B 24 cones sealed to each end. When the cones were fitted to the lids of the calorimeters the thermopile was at the correct height inside the Dewars. A water-tight seal was obtained by coating the B 24 joints with silicone grease.

The thermopile e.m.fs. were measured using a Pye Precision Decade potentiometer (type 7600), which had an overall range of 2.0 volts to 0.1 microvolts in six ranges. It was standardised using a 5 dial decade system in the battery circuit and the standard cell voltage was preset with a divider calibrated from 1.01800 to 1.01900 volts in steps of 10 microvolts. A switch incorporated in the circuit enabled internal checking

of the voltage of the standard cell. Any spurious thermoelectric e.m.f.s. could be detected and eliminated by means of a reversing switch, although these were in all cases negligible.

A Scalamp galvanometer, (type 7904/5), was used as a null detector in conjunction with a Pye galvanometer pre-amplifier, (type 11330), and changes of 0.1 microvolts were easily detected, corresponding to a heat change of about 0.1 calories.

The heater is shown in Figure 2 . Two platinium wire loops were sealed into the flattened end of a pyrex glass tube and copper leads were soft soldered to the platinium. To the constricted end was sealed a small glass former, approximately 1" x $1\frac{1}{2}$", round which was wound about twenty windings of nichrome wire, (8 ohms per foot), the ends being spot welded to the platinium loops. The heater was insulated by dipping in a solution of formvar in ethylene dichloride.

The heating circuit was similar to that of Pitzer [19], and is shown in Figure 3 . A variable resistance, A, was used to regulate the current which was measured by determining the voltage drop across a standard 1 ohm resistance, B, using a

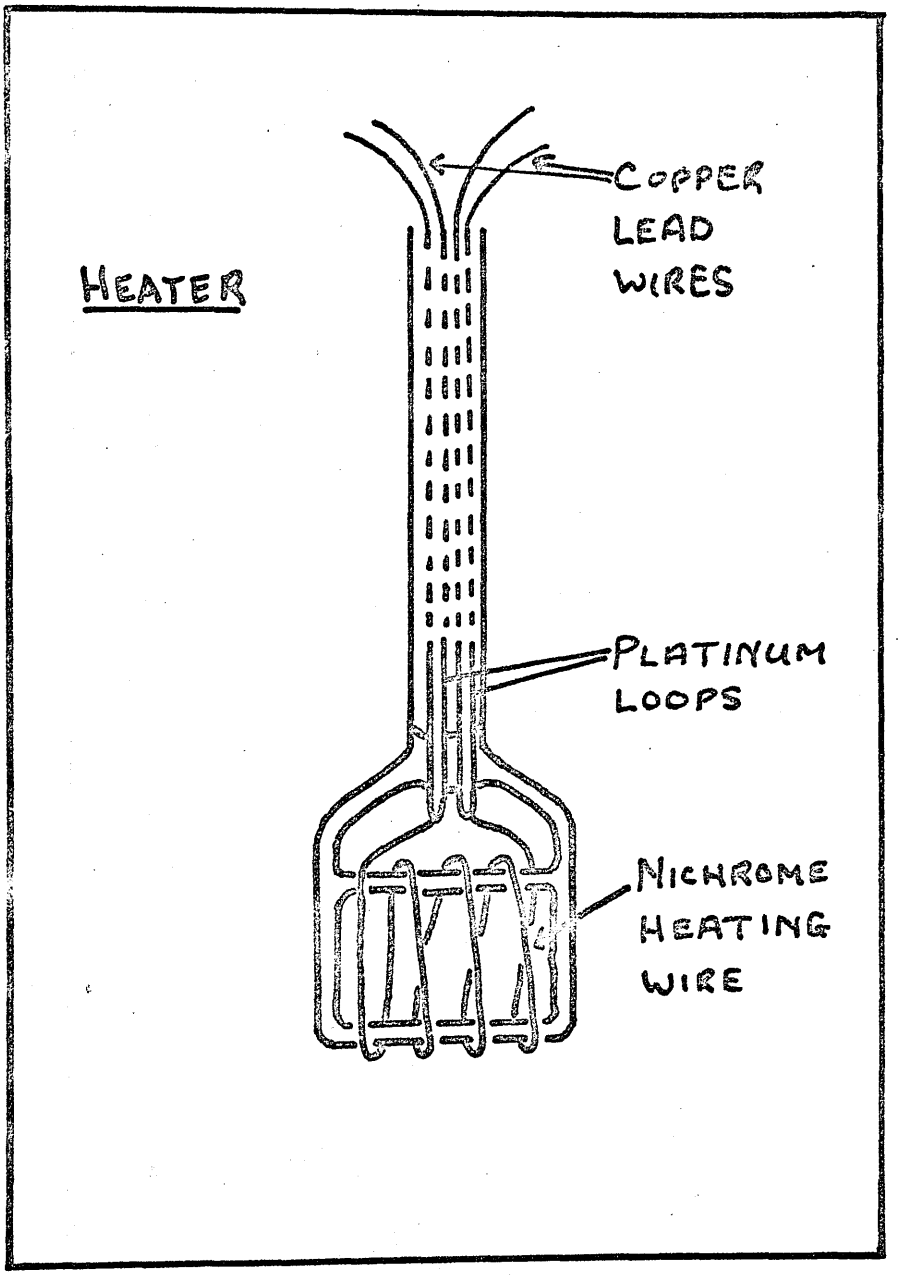

HEATER
COPPER LEAD WIRES
PLATINUM LOOPS
NICHROME HEATING WIRE

Fig. 2.

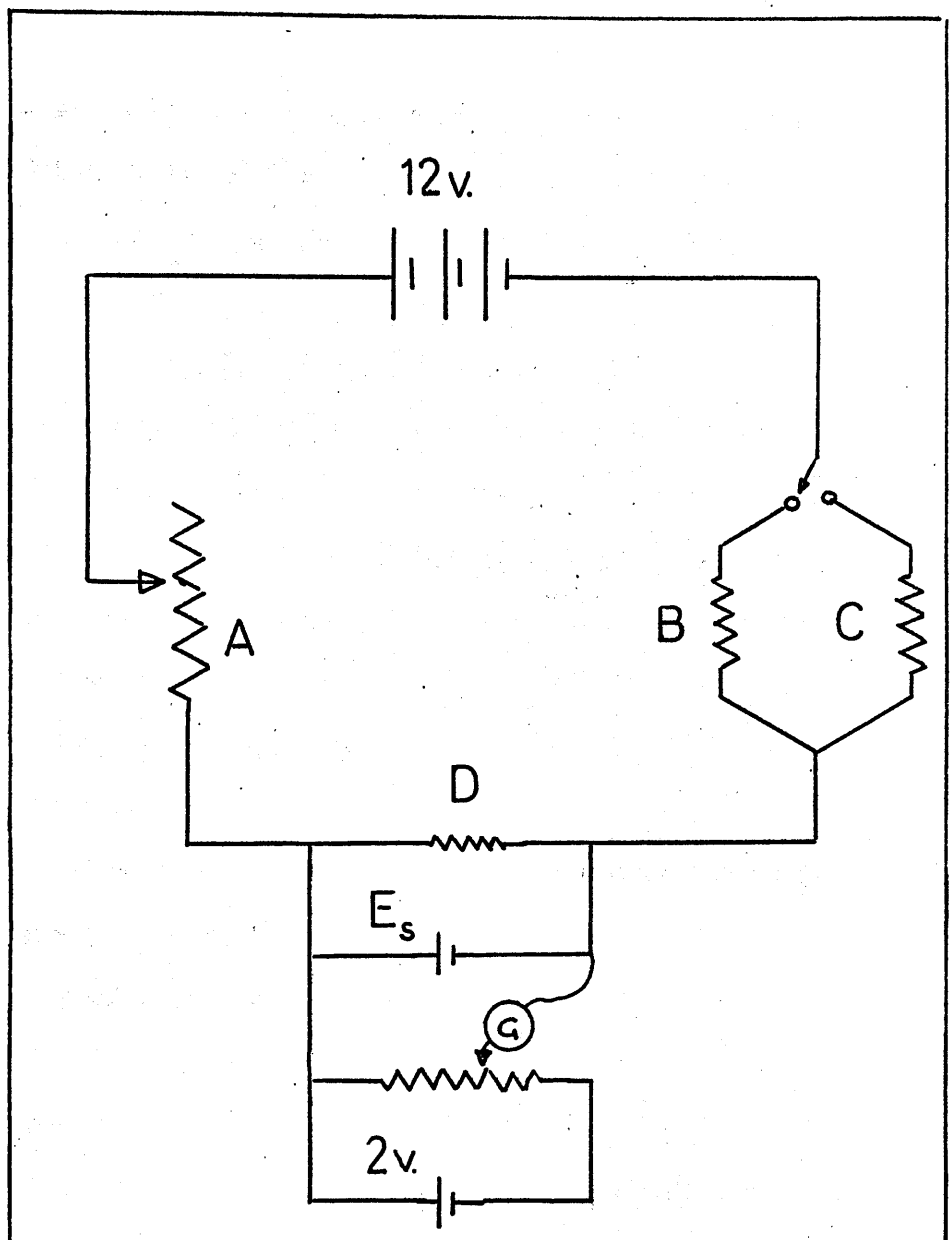


Fig. 3.

Cambridge slide-wire potentiometer. By means of a dummy resistance, equal to that of the heater, the 12 volt battery was allowed to settle down before being used in the heating circuit.

The mixing device is shown in Figure 4 . It consisted of a glass tube, of over 10 ml. capacity, which could be sealed at both ends by rubber bungs cemented on to perspex discs. The perspex discs were attached to nylon threads which were led out of the calorimeter through the glass tube supporting the mixing device. During an experiment, the contents of the mixing device could be emptied into the Dewar by pulling on the nylon threads.

The first differential thermistor calorimeter is shown in Figure 5 . Although much smaller, it was essentially the same in design as the thermocouple calorimeters. The Dewar flasks were of 500 ml. capacity and again were cemented into brass containers. To achieve better thermal insulation, a solid, cylindrically shaped teflon bung, 4 cm. in length, was cemented to the underside of each lid instead of perspex. The mixing device and heater were exactly the same in design as those previously described. To facilitate its accommodation into the much smaller Dewar, the heater was slightly modified

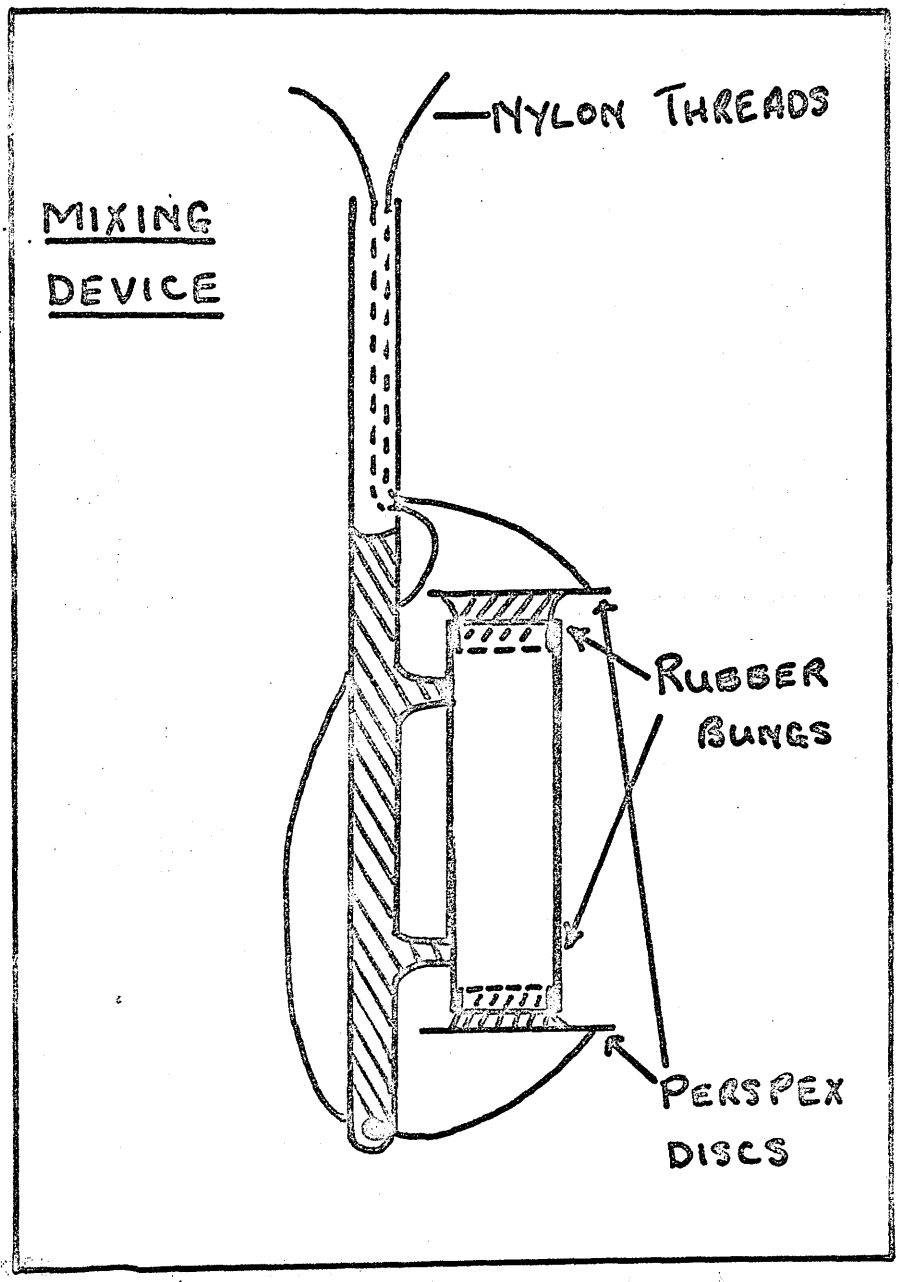
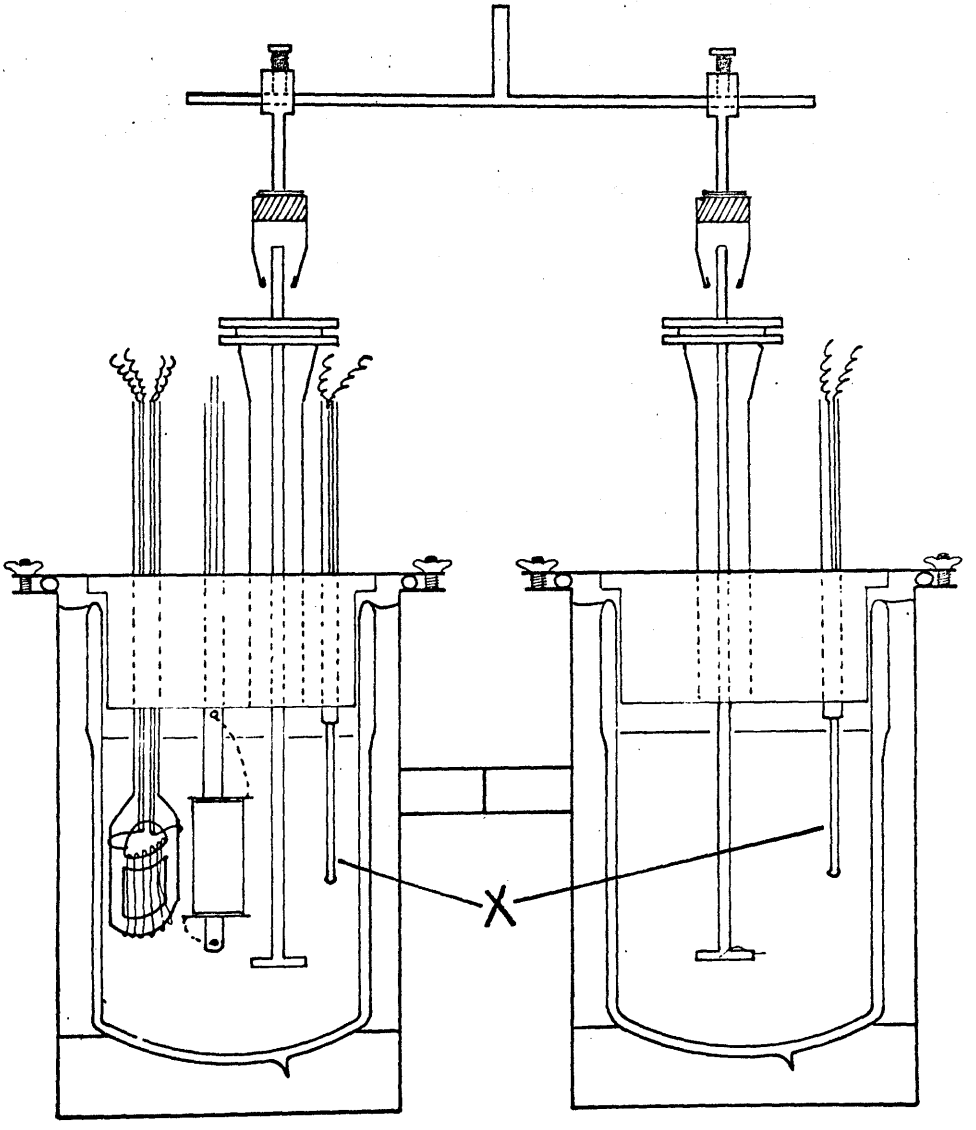


Fig. 4.



Thermistor Calorimeter

Fig. 5

by bending the glass former such that it was parallel with the walls of the flask. In this way the heater could be positioned very close to the Dewar thereby leaving the maximum amount of space to accommodate the other pieces of apparatus.

In place of the thermocouple, a pair of matched thermistors X in figure, (Stantel, Type P 15 MP), of resistance 100,000 ohm, (temperature coefficient of resistance 4% per °C.), were used as the sensing elements. These were incorporated in two arms of a wheatstone bridge, as show in Figure 6 , the other two arms of similar resistance,being high quality Helipot potentiometers. Capacity effects were balanced out by means of two 5 - 50 pF. variable condensers in parallel with the Helipots.

The bridge was energised by a stablised 1 volt a.c. signal of frequency 1000 c.p.s. The out - of - balance signal was amplified by means of a high - gain amplifier and the output was fed to a d.c. amplifier coupled to a 1 m.v. fast - response chart recorder (Honeywell Controls). The sensitivity of the bridge could be varied by means of an adjustable gain control. Since the high - gain a.c. amplifier did not incorporate a phase - conscious synchronous detector, the out - of - balance signal was always positive with respect to the balance-point signal,

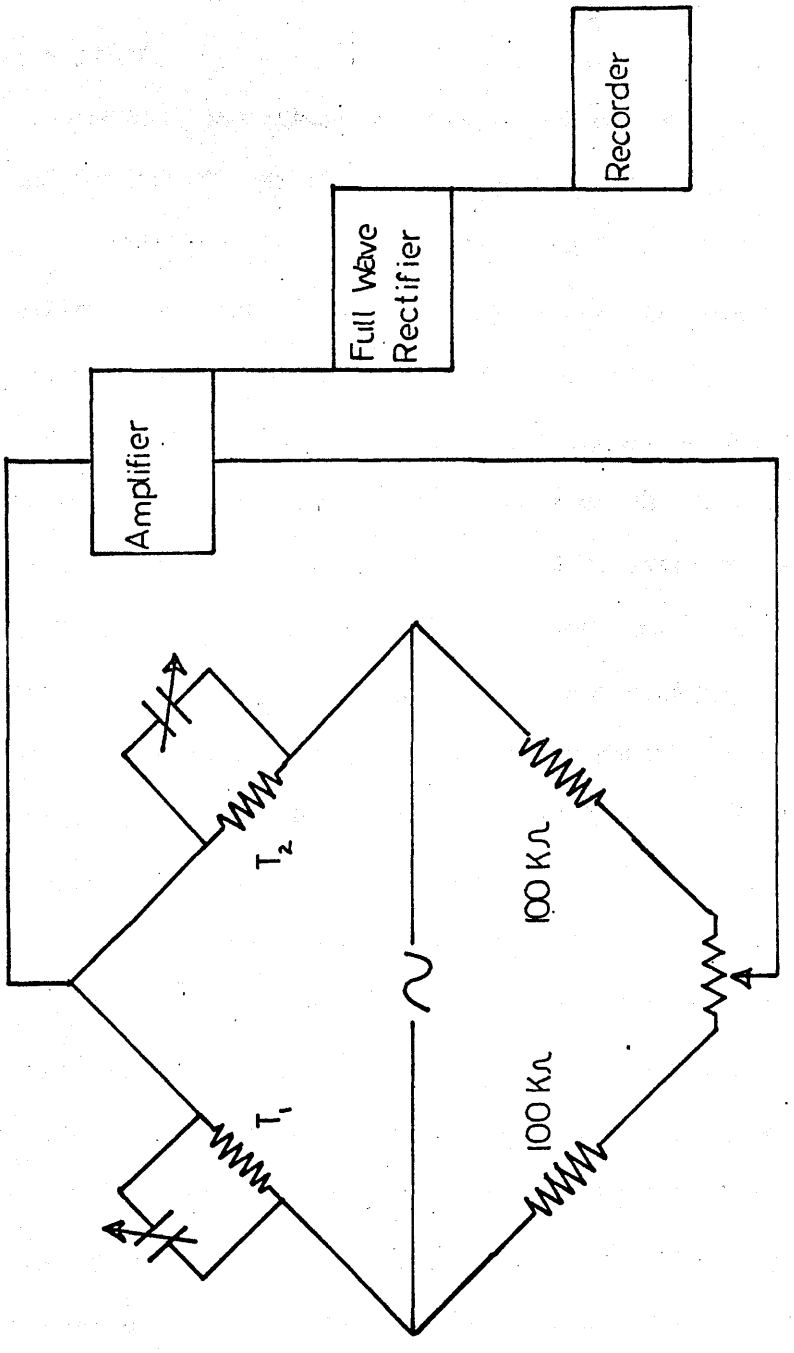


Fig. 6

and the recorded signal passed through a minimum at the balance - point.

To test the linearity of the recorded signal, high quality 100,000 ohm resistors together with high quality variable resistors were substituted in place of the thermistors, and Figure 7 shows a typical plot of output signal vs. resistance change obtained during testing. Within the region AB the output was proportional to the resistance difference between the two arms of the bridge and, therefore, the signal in this region could be used as a direct measure of the temperature difference between the calorimeters when the thermistors were incorporated in the bridge. Position A corresponded to the bridge being about 6 mV. out of balance. All heat measurements were carried out within the output range A B.

Although the noise level was sufficiently low to enable temperature differences of about 10^{-5} C, corresponding to 3×10^{-3} calories, to be detected, the most sensitive region of the bridge, which is theoretically at the balance - point, could not be utilised as a result of the above method of signal amplification. To overcome this problem a second bridge was constructed in which the high - gain a.c. amplifier

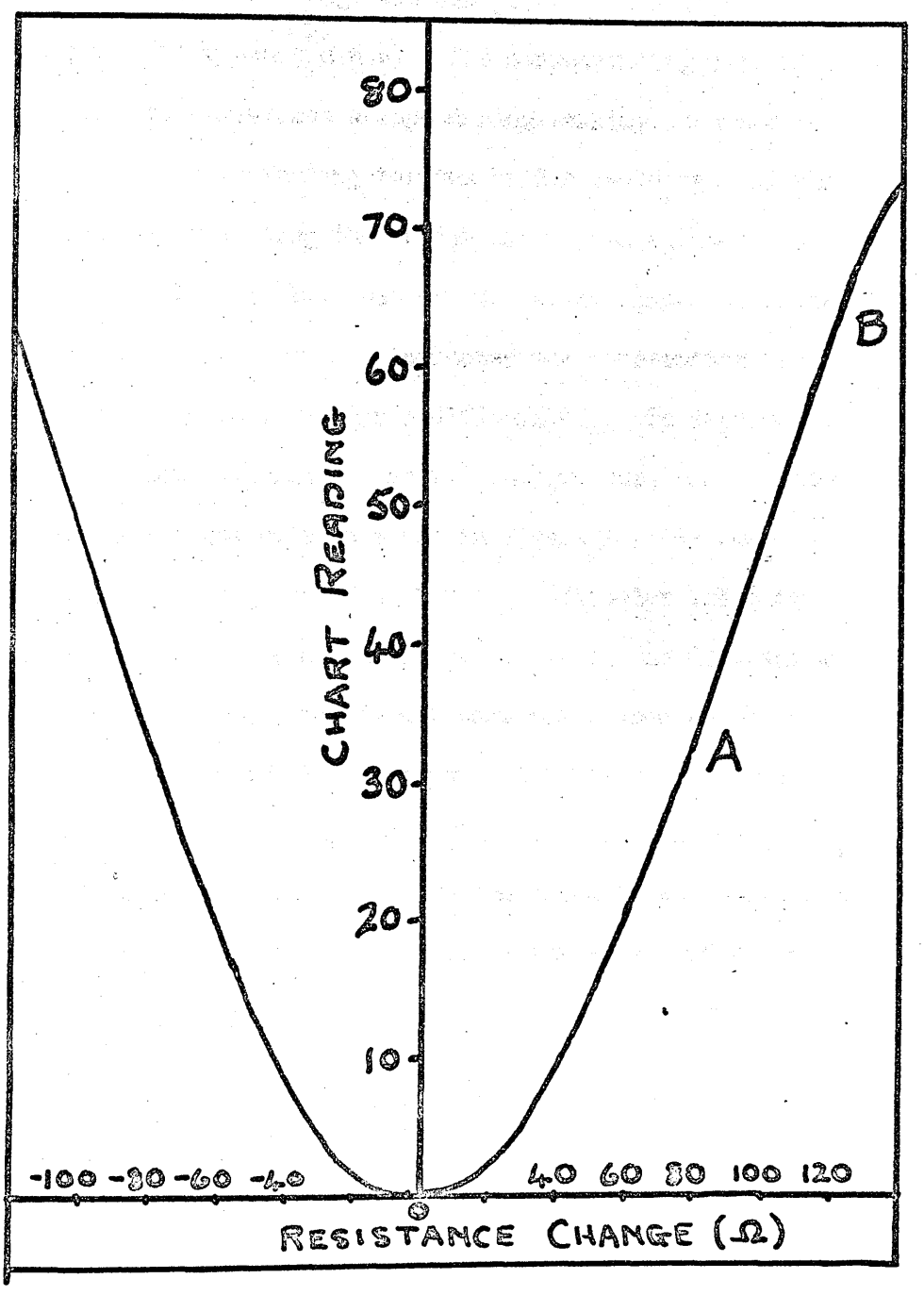

80
70
60
50
40
30
20
10
CHART READING
B
A
-100 -80 -60 -40
40 60 80 100 120
RESISTANCE CHANGE (Ω)

Fig 7.

incorporated a phase - conscious synchronous detector. In this case the bridge was energised by a stabilised 1 volt a.c. signal of frequency 800 c.p.s. The corresponding plot of output signal vs. resistance change during testing is shown in Figure 8 , illustrating how the bridge could be used throughout its range, including the region around the balance - point.

To make full use of the better linearity offered by this bridge a third calorimeter was constructed similar to the second except for two modifications. To improve the flow characteristics within the calorimeter, a new heater was constructed and this is shown in Figure 9 . It consisted of a hollow pyrex glass tube, 1 cm . in diameter and 6 cm . in length attached to a similar tube, 0.7 cm. in diameter and 12 cm. in length. The larger tube was closed at the bottom end except for a small hole through which the platinium heating wire, (42 s.w.g.), was led. The wire was then wound round the larger tube and passed through another small hole near the junction of the tubes. At both holes enamelled copper lead wires were attached to the platinium and were then led up inside the heater and out of the calorimeter. The holes were sealed with araldite and the heater insulated by painting with a

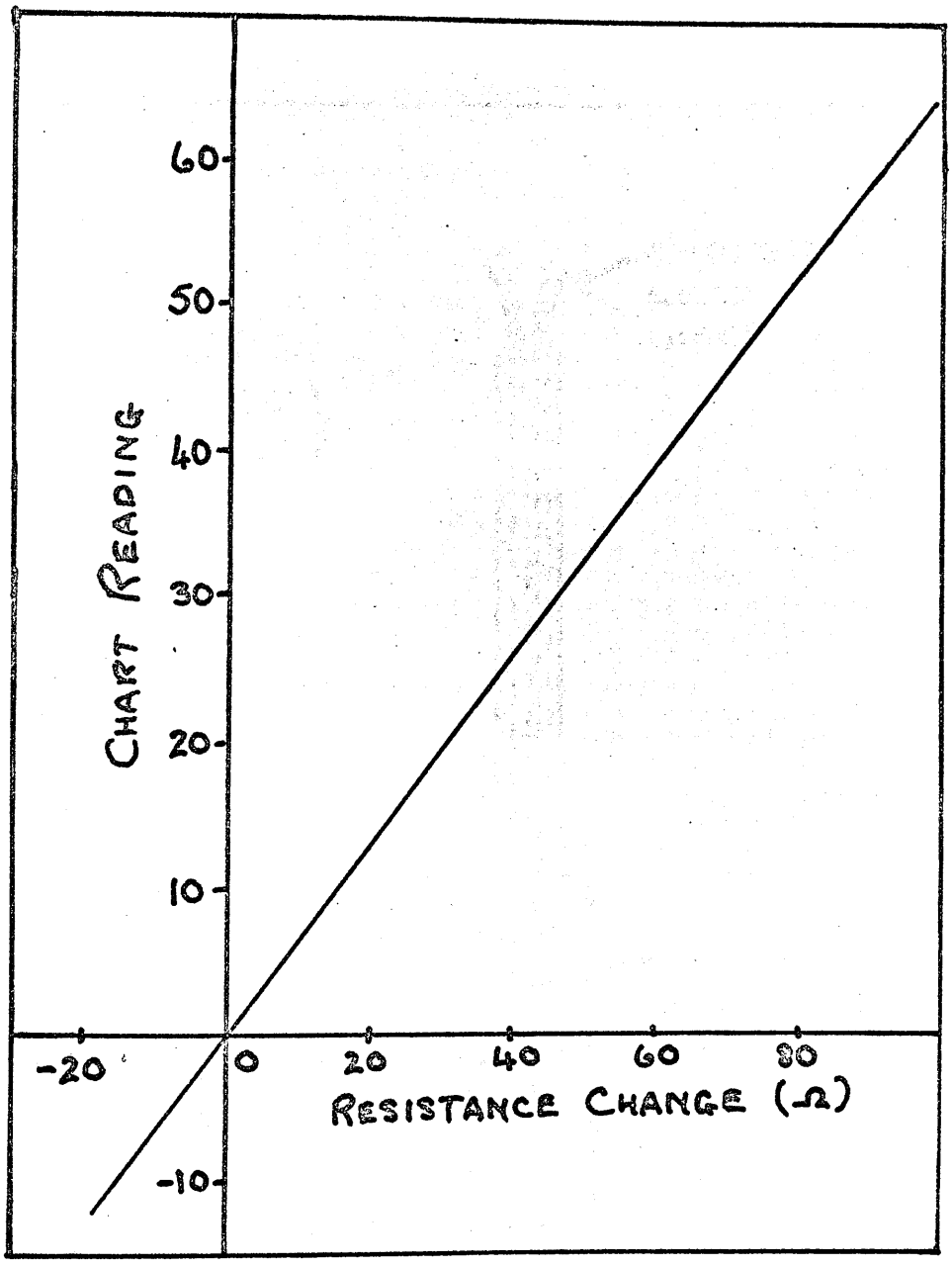

60
50
40
30
20
10
-10
CHART READING
-20
0
20
40
60
80
RESISTANCE CHANGE (Ω)

Fig. 8.

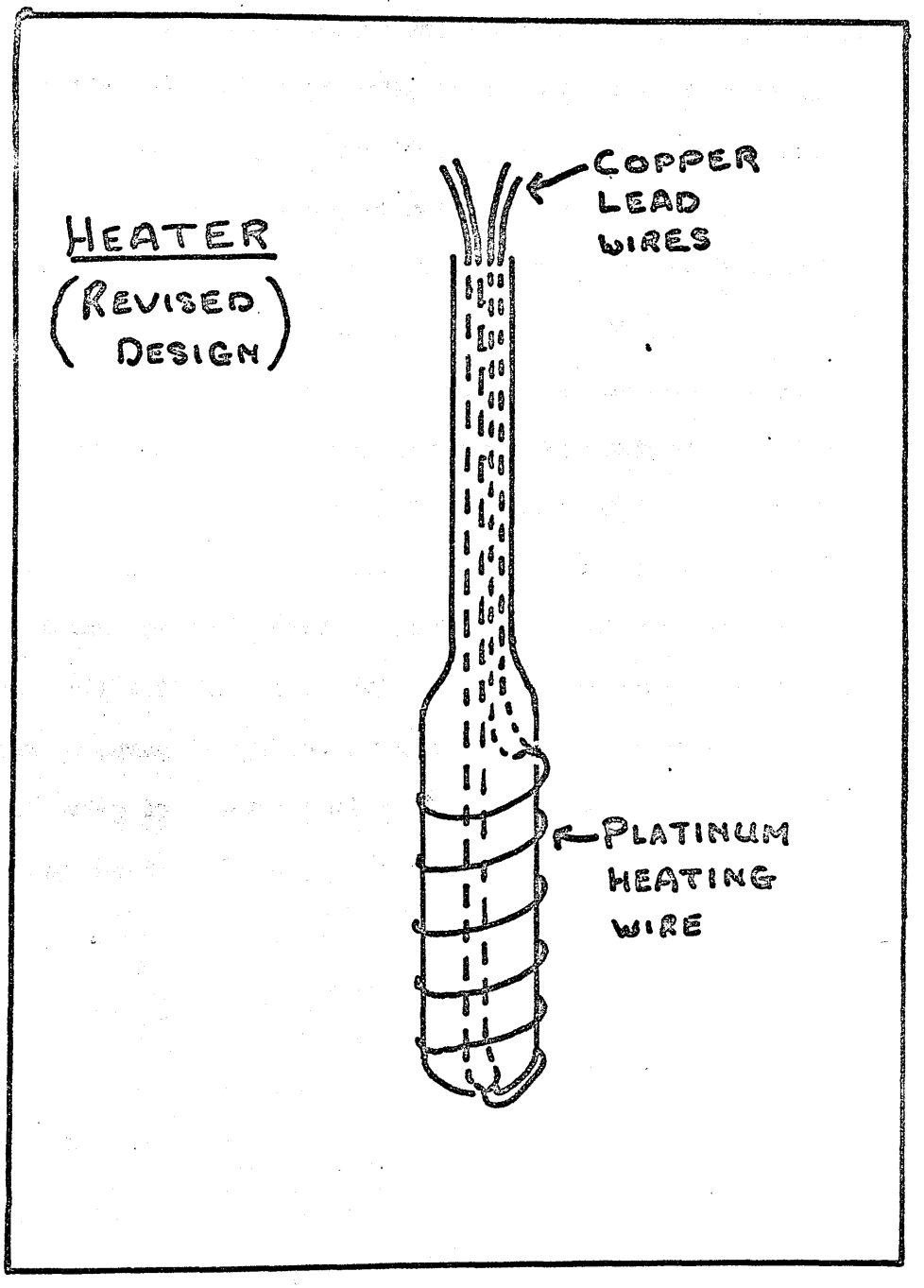

HEATER
(REVISED DESIGN)
COPPER LEAD WIRES
PLATINUM HEATING WIRE

Fig. 9.

solution of araldite in ethanol. The second modification was to incorporate a heater and a mixing device into each lid. This enabled each calorimeter to be used in turn to obtain heat measurements, the other being used as the reference.

It was found necessary, in the case of the thermistor calorimeters to fix the mixing device, heater etc. to the lids with plasticine and to adjust their positions, until optimum stirring conditions inside the calorimeters were obtained, before sealing them permanently with araldite.

For each of the differential thermistor calorimeters, the heating circuit was designed such that an electric timer, (Ericson Interval Timer), could be synchronised with the heater on - off switch. An alternative method of timing the current was to manually operate a Pye stop-clock. Tests were carried out using both methods simultaneously, consecutive results being shown in Table 1.

TABLE 1.

	Manual Timing (secs.)	Timer (secs.)
(a) Clock hand initially moving through zero		
	120	120.094
	120	120.091
	60	60.047
	60	59.955
	60	60.015
	60	60.055
(b) Clock hand initially stationary		
	60	59.995
	60	60.000
	60	59.962
	120	119.975
	120	120.010

The accuracy limits of approximately $\pm$ 0.1% when timing manually were considered low enough to enable this more convenient method to be used.

The calorimeters were completely immersed in a thermostat which was maintained at $25^{\circ} \pm 0.01^{\circ}C$ using a large capacity mercury - toluene regulator fitted with a Sunvic proportionating head(Type Tol 3B) and an A.E.I. electronic relay (Type EA4T).

EXPERIMENTAL PROCEDURE.

Thermocouple Calorimeter.

The sensitivity of the calorimeter was tested by determining the heat of solution of potassium chloride in water. Distilled water at 25°C was weighed into the calorimeter and two to three grams of potassium chloride were weighed into the mixing device, which was then sealed. The lids were screwed down and the thermopile inserted into the greased B 24 sockets. The calorimeter was then placed in the thermostat.

After stirring for at least two hours, and sometimes overnight, readings were taken every minute. When a steady change of e.m.f. had been obtained, heat was introduced by switching the heater into the circuit. The voltage drop across the standard 1 ohm resistance was measured every minute to ensure a steady heating current. After the heater had been turned off and the e.m.f. had settled down to another steady rate of change, the mixing device was opened and two to three minutes were usually necessary for the potassium chloride to dissolve completely. When the change in e.m.f. had once

more become steady, the water equivalent was again determined by heating electrically.

Thermistor Calorimeters.

The sensitivity of the first calorimeter was tested by determining the heat of solution of potassium chloride in water in a manner similar to that already described. As a result of the increased sensitivity offered by this calorimeter, it was only necessary to add approximately 0.05 gms. of potassium chloride from the mixing device.

The heat of ionisation of water was used to test the sensitivity of the second thermistor calorimeter. The classical method of determining ΔH for the reaction,

$$H^+ + OH^- \rightleftharpoons H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

is to measure the heat of neutralisation of a strong acid with a strong base. Sodium Hydroxide solutions were sealed in the mixing device and the experimental heat change measured when they were mixed with dilute acid solutions contained in the Dewar. A stoichiometric excess of base was used to avoid any heat effects from the neutralisation of carbonate in the base.

Determination of the Heats of Complex Formation.

In order to determine the heats of complex formation, potassium glycinate solutions were pipetted into the mixing device and added to the metal solutions in the Dewar. Suitable final pHs. were obtained by adding known volumes of standard hydrochloric or perchloric acid to the Dewar solution. The heat of dilution of the metal solutions was assumed to be zero [23], but it was necessary to determine the heat of dilution of the potassium glycinate solutions for each run. This was done by measuring the heat obtained on mixing the same volume of potassium glycinate into a solution of the same ionic strength as that of the metal solution, but without the metal present, containing the same amount of acid. The pH of all solutions were measured at the end of each run using an E.I.L. Direct Reading Meter (Model 23A).

Precautions were taken in all experiments to exclude carbon dioxide from the solutions. Nitrogen was blown into both the mixing device and the Dewar while they were being filled. Nitrogen was also blown into the calorimeter while the lid was being screwed down and the open end of the tube, through which the nylon threads from the mixing device protruded, was sealed with plasticine.

Evaluation of Heat Changes.

The method used for the evaluation of water equivalents and the heats of solution and formation was that of Eitel [36]. In figure 10, which is a graphical reproduction of part of one of the experiments, e.m.f. is plotted against time. This was divided into three periods, the Anterior, the Experimental and the Rating periods. The first reading was designated θ_o at time T_o, and at T_i, where the reading was θ_i, the heater was switched on or mixing was affected. The rate of change, V_a, was given by $(\theta_o - \theta_i) / (T_i - T_o) \mu v.t^{-1}$, and the average reading in this period was $\theta_a = \frac{1}{2} (\theta_o + \theta_i) \mu v.$

The experimental period stretched from T_i to T_e, the corresponding readings being θ_i and θ_e. The heat effect was exhausted by T_e and the curve entered the rating period.

The rating period was treated in the same manner, the rate of change V_r and the average reading, θ_r, were given by $(\theta_e - \theta_1) / (T_1 - T_e) \mu v.t^{-1}$ and $\frac{1}{2} (\theta_e + \theta_1) \mu v.$ respectively.

The Regnault - Pfaundler formula was then applied to correct the experimental heat change for any variation in slopes of the anterior and rating periods. The correction applied to $(\theta_e - \theta_i) \mu v.$ was

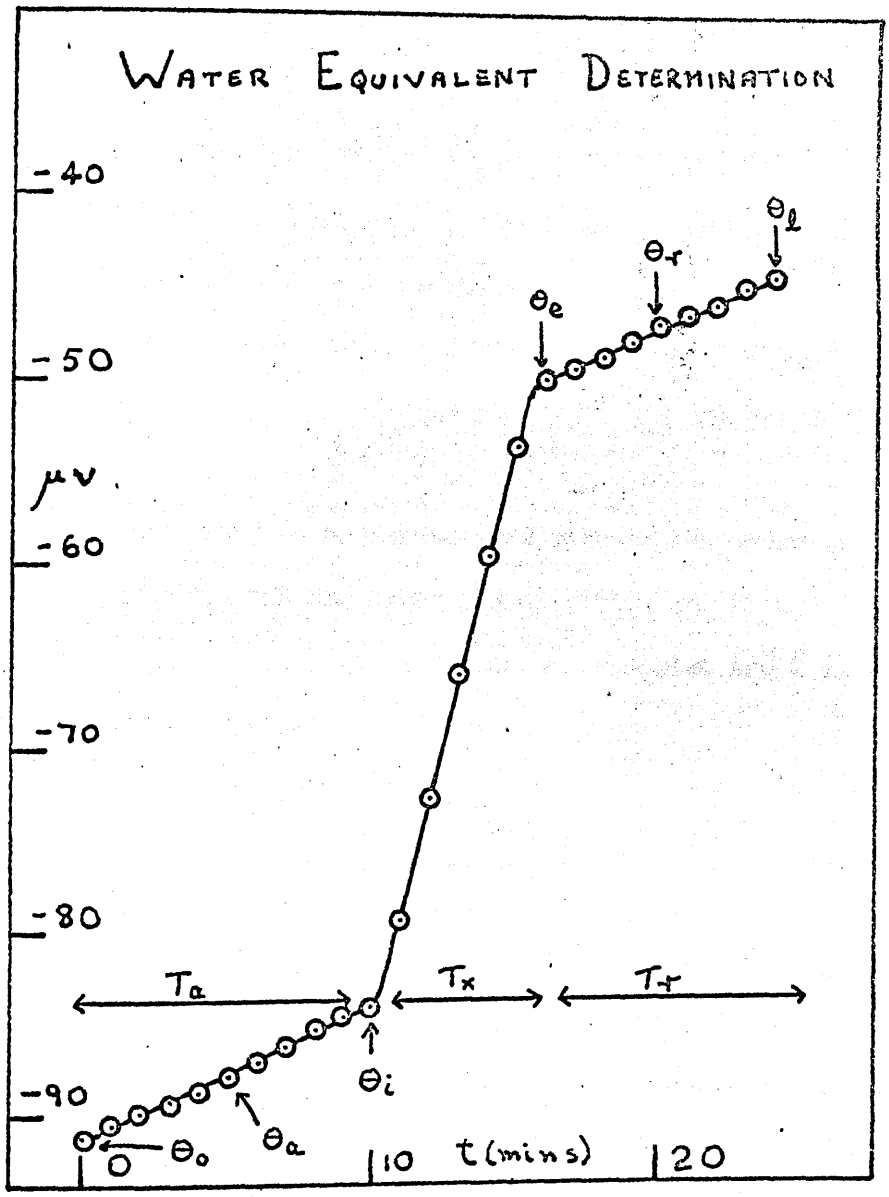

WATER EQUIVALENT DETERMINATION
-40
-50
μv
-60
-70
-80
-90
θl
θr
θe
θi
θa
θo
Ta
Tx
Tr
0
10
t(mins)
20

FIG. 10

$$\delta\theta = T_x V_a + (V_r - V_a)/(\theta_r - \theta_a).\left[\tfrac{1}{2}(\theta_o + \theta_i) + \sum_{T_i}^{T_o - 1}\theta - T_x\theta_a\right]$$

and the corrected heat change was given by $\Delta\theta = (\delta\theta + \theta_o - \theta_i)\mu v.$ Multiplication of $\Delta\theta\mu v.$ by the water equivalent (in cals./μv.) gave the experimental heat change, -Q cals.

For the thermistor calorimeters chart readings were substituted for e.m.f. readings, otherwise the treatment was identical.

Anterior and rating periods were of the order of 5 to 10 minutes and the experimental period was from 2 to 3 minutes for the dissolution of potassium chloride and 2 minutes for complex formation.

Results.

Data available for the heat of solution of potassium chloride have been reviewed by Mishenko and Kaganovitch [37] and Rossini [38]. Direct comparison with results from other workers is made difficult because of the wide variety of concentrations and temperatures used. Davies, Singer and Staveley [20] have corrected previous data to a standard dilution of 1 mole of potassium chloride to 167 moles of water at 25°C. In this study, the results were corrected to Staveley's ratio using Rossini's tables [39]. The results for the thermopile calorimeter are listed in Table II and for the thermistor calorimeter in Table III.

TABLE II.

Run	Wt.KCl. (gms.)	Wt. H_2O (gms.)	-Q (Cals.)	$-\Delta H$ (k.cal.mole^{-1}).
1.	2.3487	1,181.39	131.7	4.21
2.	2.9994	1,189.92	165.7	4.12
3.	2.8924	1,172.04	158.7	4.10
4.	2.9975	1,186.90	170.0	4.23

Mean $-\Delta H = 4.17 \pm 0.07$ k.cal.mole^{-1}.

TABLE III

Run	Wt.Kcl. (gms.)	Wt.H_2O (gms.)	-Q (Cals.)	$-\Delta H$ (k.cal.mole^{-1}).
1.	.0497	294.38	2.78	4.17
2.	.0476	322.38	2.65	4.15
3.	.0456	287.56	2.55	4.16

Mean $-\Delta H = 4.16 \pm 0.01$ k. cal. mole^{-1}.

The mean values of 4.17 and 4.16 k. cal. mole^{-1} compare well with those of Staveley [20], 4.184, and Rossini [39], 4.194 K.cal. mole^{-1}.

The values in the literature for the heats of ionisation of water refer to a variety of ionic strengths and temperatures. Rossini [40] and Pitzer [19] corrected these values to zero ionic strength and 25°C. Recently estimations were carried out at low ionic strength with a refined correction for heat of dilution [41] and it has been shown [42] that the ΔH_o value is independent of whether hydrochloric or perchloric acid was used. In testing the thermistor calorimeter the heat changes were limited to approximately the same as these expected in subsequent complex formation experiments. The results are shown in Table IV.

TABLE IV

Run	$-Q$ (cal.)	$-\Delta H_I$ (k.cal.mole^{-1})	δ cal.	$-\Delta H_o$ (k.cal.mole^{-1})
3.	5.47	13.10	38	13.06
4.	5.56	13.31	38	13.27
5.	4.15	13.25	32	13.23
6.	4.12	13.12	32	13.08
7.	4.33	13.83	33	13.80
8.	4.28	13.68	38	13.64
9.	5.54	13.27	36	13.23
10.	5.57	13.34	36	13.30

Mean ΔH_o = 13.33 $\pm$ 0.20 k.cal. mole^{-1}.

Where ΔH_I and ΔH_o are the heats of water formation at the ionic strength studied and at zero ionic strength respectively. The mean of the values is comparable to those obtained by most workers, whose results are summarised in Table V.

TABLE V

Heat of Ionisation of Water.

Reaction	$-\Delta H_o$ (k.cal.mole^{-1})	Ref.
HCl + NaOH	13.363	19
HCl + NaOH	13.320	43
HCl + NaOH	13.336	44
HCl + NaOH	13.356	20
$HClO_4$ + NaOH	13.334	45
$HClO_4$ + NaOH	13.335	42
HCl + NaOH	13.34	42
$HClO_4$ + NaOH	13.33	this work.

All the results for association experiments reported in this thesis were obtained with the second thermistor calorimeter, the ionic strength being maintained at 0.1 with potassium chloride.

If an appreciable excess of metal ion was used in the association experiments and the pH was controlled, conditions could be chosen such that only the 1:1 complex, MA^+, was formed. The concentration of ionic species were calculated from the following equations:

The dissociation constants of glycine,

$$k_1 = \{H^+\}[HA]/[H_2A^+]f_1 \quad \text{.....(9)}$$

and $$k_2 = \{H^+\}[A^-]f_1/[HA], \quad \text{.....(10)}$$

(where braces denote activities)

The association constant of the complex,

$$K = [MA^+]/[M^{2+}][A^-]f_2, \quad \text{.....(11)}$$

total acid, $T_a = [H_2A^+] + [HA] + [A^-] + [MA^+]$ .....(12)

and total metal, $T_m = [MA^+] + [M^{2+}]$ .....(13)

$$= [MA^+] + [MA^+]/K[A^-]f_2 \quad \text{.....(14)}$$

$$= [MA^+] + [MA^+]/Kf_2(T_a - [H_2A^+] - [HA] - [MA^+]) \quad \text{...(15)}$$

Multiplying equation(15)by $(T_a - [H_2A^+] - [HA] - [MA^+])$

and omitting concentration brackets for convenience gave

$$T_m Kf_2 (T_a - H_2A^+ - HA - MA^+) = MA^+ Kf_2(T_a - H_2A^+ - HA - MA^+) + MA^+ \quad \text{...(16)}$$

Putting $(T_a - H_2A^+ - HA) = v$ and rearranging gave,

$$T_m Kf_2 v - T_m Kf_2 MA^+ = MA^+ Kf_2 v - (MA^+)^2 Kf_2 + MA^+$$

i.e. $$Kf_2(MA^+)^2 - MA^+ \cdot [Kf_2(T_m + v) + 1] + T_m Kf_2 v = 0 \quad \text{.....(17)}$$

Putting $[MA^+] = 0$ in equation (16) for the first cycle enabled a value for $[MA^+]$ to be obtained from equation (17). This calculated value was then substituted into equation (16) and the calculation repeated until consecutive solutions of equation (17) were identical. The concentrations of the other ionic species were then obtained from equations (13), (11), (10) and (9).

The above treatment represents a rigorous solution of the problem. In order to facilitate the successive approximation procedure, a preliminary value for $[MA^+]$ was substituted into equation (16) before the cycling process was started. This preliminary value was calculated from the following equations, (omitting concentration brackets)

$$\begin{aligned} T_a - MA^+ &= H_2A^+ + HA + A^- \\ &= \{H^+\} HA/k_1f_1 + HA + k_2HA/\{H^+\}f_1 \\ &= HA\left[\{H^+\}/k_1f_1 + 1 + k_2/\{H^+\}f_1\right] \quad \ldots\ldots\ldots (18) \end{aligned}$$

Substituting $[MA^+] = 0$ in equation (18) enabled a value for $[HA]$ to be obtained.

Since it was assumed in this treatment that $[MA^+] = 0$ for the first cycle, the derived value of $[HA]$ was too large and hence $[A^-]$ and $[MA^+]$, calculated from equations (10) and (14) respectively, were also too large. Substitution of this calculated value for $[MA^+]$ in equation (18) reversed the above results and gave values which were too small. Successive cycling by this preliminary approximation procedure gave, therefore, an oscillating approach to a constant $[MA^+]$ value, and this value was substituted into the main calculation.

By conducting experiments with an appreciable excess of ligand and controlling the pH to a rather higher value, the predominant complex formed was the 1:2 species MA_2. Both the copper and the cobalt complexes were studied under these conditions and the concentrations of ionic species were calculated by extending the procedure already described to include the complex MA_2 as well as MA^+. It was not possible to study the zinc complexes in this manner since the solution in this case had to be kept below about pH7 to prevent precipitation of zinc hydroxide.

The measured heat change, Q, was expressed by,

$$Q = Q' + \left[q(1) + q(2) + q(3) + q(4)\right] \quad \ldots\ldots\ldots\ldots\ldots (19)$$

where Q' was the contribution from the heat of complex formation, $q(1)$, the heat of dilution of the potassium glycinate, $q(2)$, the heat due to formation of water, and $q(3)$ and $q(4)$, the heat contributions from changes in the ligand equilibria. The value of $q(1)$ was obtained from a blank run carried out for each experiment.

Knowing the pH of the blank solutions, pH_B, concentrations of the acid species $[A^-]_B$, $[H_2A]_B$ and $[HA]_B$ were calculated from the dissociation constants of glycine, $k_1 = 4.46 \times 10^{-3}$ moles $l.^{-1}$ and $k_2 = 1.67 \times 10^{-10}$ moles $l.^{-1}$[46], and from the expression for the total acid,

$$T_a = [A^-] + [HA] + [H_2A^+]$$
$$= [A^-] + \{H^+\}[A^-]f_1/k_2 + \{H^+\}^2[A^-]f_1/k_1k_2f_1$$

hence $[A^-] = T_a/(1+\{H^+\}f_1/k_2 + \{H^+\}^2/k_1k_2)$.

The corresponding concentrations in the metal complexing experiments, $[A^-]_c$, $[HA]_c$ and $[H_2A^+]_c$, (at pH_c), were calculated by the method already described and the heat contributions, $q(3)$ and $q(4)$ were evaluated from

the appropriate heats of protonation [46],

$$A^{-} + H^{+} \rightleftharpoons HA, \quad \Delta H_{Ass} = -10.80 \text{ k.cal.mole}^{-1},$$

and $$HA + H^{+} \rightleftharpoons H_2A^{+}, \quad \Delta H_{Ass} = -0.95 \text{ k.cal.mole}^{-1}.$$

The heat contribution, $q(2)$, was calculated from pH_B and pH_C using Staveley's value, $-\Delta H = 13.36$ k. cal. mole^{-1}, for the heat of formation of water.

With a knowledge of $q(1)$, $q(2)$, $q(3)$ and $q(4)$, the experimental heat due to complex formation, Q', was calculated from equation (19). The heat of complex formation, ΔH_I k.cal.mole^{-1}, was then calculated for an ionic strength of 0.1 and the thermodynamic heat of complex formation, ΔH_o k.cal.mole^{-1}, was derived from the equation,

$$\Delta H_o = \Delta H_I + 2.303RT^2 \frac{3}{2} \left(\frac{1}{D} \frac{dD}{dT} + \frac{1}{T} \right) \log f_2^2 , \quad \text{(Ref.47)}$$

in which the values of D, the dielectric constant of water, were those of Akerlof [48].

The results for the heats of formation of cobalt (11), copper (11), and zinc (11) glycinate complexes appear in Tables VI to XI.

Table VI.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	-Q (cal.)	-Q' (cal.)
1	300	11.8	.127	1.503	1.225
2	300	15.3	.112	1.712	1.186
3	300	14.9	.122	1.822	1.057
4	300	14.1	.122	1.715	1.212
5	300	17.6	.103	1.809	1.044

Heat of Formation of the Cobalt Glycinate Complex, MA^+.

Molar Concentrations

Run	$T_m \cdot 10^3$	$T_g \cdot 10^3$	$[MA^+] \cdot 10^3$
1	6.5480	1.6760	1.4357
2	9.8220	1.6760	1.3597
3	8.1850	1.6760	1.2773
4	9.8220	1.6760	1.3709
5	8.1850	1.6760	1.2773

Run	ΔH_I (k.cal.mole^{-1}.)	ΔH_o (k.cal.mole^{-1}.)
1	-2.84	-2.18
2	-2.91	-2.25
3	-2.75	-2.09
4	-2.95	-2.29
5	-2.72	-2.06

Mean ΔH_o = -2.18 ± 0.05 k.cal.mole^{-1}.

Table V11.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	-Q (cal.)	-Q' (cal.)
1	300	25.0	.126	3.148	3.421
2	300	27.5	.114	3.136	3.296
3	300	29.2	.109	3.186	3.367
4	300	27.5	.116	3.186	3.473
5	300	31.6	.101	3.193	3.482
6	300	26.4	.119	3.137	3.412

Heat of Formation of the Copper Glycinate Complex, MA^+.

Molar Concentrations

Run	$T_m \cdot 10^3$	$T_a \cdot 10^3$	$[MA^+] \cdot 10^3$
1	5.2567	1.6760	1.6071
2	6.3080	1.6760	1.5721
3	6.3080	1.6760	1.5786
4	5.2567	1.6760	1.6114
5	4.2053	1.6760	1.6118
6	4.2053	1.6760	1.6075

Run	ΔH_I (k.cal.mole^{-1}.)	ΔH_o (k.cal.mole^{-1}.)
1	-7.10	-6.44
2	-6.99	-6.33
3	-7.11	-6.45
4	-7.18	-6.52
5	-7.20	-6.54
6	-7.07	-6.41

Mean ΔH_o = -6.45 ± 0.04 k.cal.mole^{-1}.

Table V111.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	-Q (cal.)	-Q' (cal.)
1	300	27.2	.112	3.050	.354
2	300	28.5	.107	3.049	.365
3	300	66.6	.122	8.122	.082
4	300	63.7	.124	7.899	.225
5	300	69.5	.117	8.127	.100

Heat of Formation of the Zinc Glycinate Complex, MA^+.

Molar Concentrations

Run	$T_m \cdot 10^3$	$T_a \cdot 10^3$	$[MA^+] \cdot 10^3$
1	6.8225	12.1730	2.7406
2	6.3032	12.3290	2.8293
3	9.1000	2.5000	0.8567
4	9.1000	2.5000	1.9822
5	9.1000	2.5000	0.8954

Run	ΔH_I (k.cal.mole^{-1}.)	ΔH_o (k.cal.mole^{-1}.)
1	-3.97	-3.31
2	-4.05	-3.39
3	-3.20	-2.54
4	-3.78	-3.12
5	-3.71	-3.05

Mean ΔH_o = -3.08 ± 0.17 k.cal.mole^{-1}.

Table IX.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	-Q (cal.)	-Q' (cal.)
1	300	78.9	.121	9.543	2.321
2	300	76.1	.128	9.740	2.568
3	300	74.8	.129	9.646	2.427
4	300	77.0	.128	9.848	2.301
5	300	82.9	.117	9.696	2.518
6	300	79.9	.123	9.832	2.479

Heat of Formation of the Cobalt Glycinate Complex, MA_2.

Molar Concentrations

Run	$T_m \cdot 10^3$	$T_a \cdot 10^3$	$[MA^+] \cdot 10^4$	$[MA_2] \cdot 10^3$
1	1.6370	6.7040	2.2380	1.3864
2	1.9644	6.7040	3.9321	1.5313
3	1.8007	6.7040	3.0826	1.4595
4	1.6370	6.7040	2.2088	1.3894
5	1.9644	6.7040	3.9321	1.5313
6	1.8007	6.7040	2.9624	1.4723

Run	ΔH_I (k.cal.mole^{-1}.)	ΔH_o (k.cal.mole.$^{-1}$)
1	-5.58	-4.92
2	-5.59	-4.93
3	-5.54	-4.88
4	-5.52	-4.86
5	-5.48	-4.82
6	-5.61	-4.95

Mean ΔH_o = -4.89 ± 0.02 k.cal.mole^{-1}.

Table X.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	-Q (cal.)	-Q' (cal.)
1	300	82.0	.156	12.797	13.202
2	300	70.8	.151	10.685	11.422
3	300	79.8	.149	11.895	12.296
4	300	84.7	.150	12.709	13.129
5	300	73.0	.146	10.664	11.276
6	300	76.4	.158	12.077	12.444

Heat of Formation of the Copper Glycinate Complex, MA_2.

Molar Concentrations

Run	$T_m \cdot 10^3$	$T_a \cdot 10^3$	$[MA^+] \cdot 10^4$	$[MA_2] \cdot 10^3$
1	3.2802	6.7040	1.6974	3.1101
2	2.6283	6.7040	$4.6597 \cdot 10^{-3}$	2.6279
3	2.9437	6.7040	$1.4856 \cdot 10^{-2}$	2.9422
4	3.2802	6.7040	1.6495	3.1149
5	2.6283	6.7040	$4.7951 \cdot 10^{-3}$	2.6279
6	2.9437	6.7040	$1.5251 \cdot 10^{-2}$	2.9422

Run	ΔH_I (k.cal.mole.$^{-1}$)	ΔH_o (k.cal.mole.$^{-1}$)
1	-14.14	-13.48
2	-14.49	-13.83
3	-13.93	-13.27
4	-14 05	-13.39
5	-14.30	-13.64
6	-14.10	-13.44

Mean ΔH_o = -13.51 ± 0.09 k.cal.mole.$^{-1}$

Table XI.

Thermodynamic Properties.

Reaction	$-\Delta G$	$-\Delta H_o$	ΔS
$Co^{2+} + G^-$	6.89	2.22	15.7
$Cu^{2+} + G^-$	11.71	6.41	17.8
$Zn^{2+} + G^-$	7.50	3.08	14.8
$CoG^+ + G^-$	5.42	2.04	11.3
$CuG^+ + G^-$	9.47	6.24	10.8

DISCUSSION:

The work done, W, in forming an ion - pair from the separate ions in solution can be written [51],

$$W = \frac{\Delta G}{N} - kT \ln 55.5 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

where N is Avagadro's number and k in the Boltzmann constant. The term $-kT \ln 55.5$ is a characteristic of reactions in aqueous solution in which the number of solute particles decreases by unity, 55.5 being the number of moles in 1000 gms. of water. Its inclusion renders K dimensionless. The forces between two oppositely charged ions in solution can be considered to be made up of long - range, or electrostatic, and short - range, or quantum mechanical terms. While the electrostatic force will be one of attraction, the quantum mechanical force may be attractive or repulsive depending upon the electronic configuration of the ions. The work term, W can therefore be considered to be composed of two parts, W_{env}, sensitive to environment and temperature, and W_{non}, insensitive to environment and independent of temperature. Equation (20) can therefore be written,

$$W = W_{env} + W_{non} = -kT(\ln K + \ln 55.5) = -kT \ln K_x \quad \ldots\ldots (21)$$

Since W_{env} , is electrostatic in origin, it will vary with temperature in the same way as the reciprocal of the dielectric constant of the solution.

For normal temperatures the variation of the dielectric constant with temperature can be expressed by the equation,

$$1/D = e^{T/\theta}/D_o ,$$

where D_o and θ are constants for the chosen solvent.

If W_{env} is proportional to $1/D$, equation (21) will have the form,

$$\ln K_x = -c \frac{a + e^{T/\theta}}{T} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22)$$

where $ca = W_{non}/k$ and $ce^{T/\theta} = W_{env}/k$

By differentiating equation (22) with respect to temperature and equating to zero $a/T^2 + (1 - T/\theta)e^{T/\theta}/T^2 = 0$

It can be shown that $\ln K_x$ will pass through a minimum at temperature T^* when,

$$T^* = \theta(1 + a/e^{T^*/\theta})$$

or $$T^* = \theta(1 + W_{non}/W^*_{env})$$

where W^*_{env} is the value of W_{env} at temperature T^*.

Thus the position of the minimum depends not on the sum $W_{non} + W_{env}$, but on their ratio.

At temperatures below T^*, K values will decrease with increasing temperature due to the tendency for thermal agitation to cause dissociation of the associated ions. At temperatures above T^*, K values will increase with temperature due to the decrease in mutual potential energy. The position of T^* may be sufficiently low to be below the freezing point of the solvent. In this case $d \ln K / dT$ will be positive over the entire temperature range where studies are possible, inferring predominately electrostatic interactions in the association. This behaviour has been noted for the alkaline earth hydroxides. McAuley [52] calculated the temperatures at which ΔH_o for some transition metal oxalates was zero and it was found to fall along the series Ni, Co and Mn. This possibly reflects the increasing B-type character with increasing atomic number in the first transition series.

Since it has been suggested that the heats of formation of complexes are related to metal - ligand bond strengths [53], and that bond strengths are increased by increasing W_{non} [16,54], the exothermicity of a reaction

would be expected to increase with T^*.
This has been shown to be so for transition metal glycinate, malonate, oxalate and β-alaninate complexes [55].

In complex formation the nitrogen atom donates its lone pair of electrons more readily than does the oxygen atom and hence forms bonds which are more covalent. This leads to a greater W_{non}, a higher T^*, and K values which decrease with increasing temperature. Uusitalo [56] has shown that when the donor atom is oxygen, the entropy term is important, but with nitrogen as donor, the enthalpy change is of greater importance. When both nitrogen and oxygen are present $T\Delta S$ and ΔH are comparable for strong complexes, but $T\Delta S$ increases in importance as the stability of the complex decreases. These points are illustrated by comparing the thermodynamic properties of the reactions between cobalt (II) and the glycinate and oxalate [57] anions which are given in Table XII.

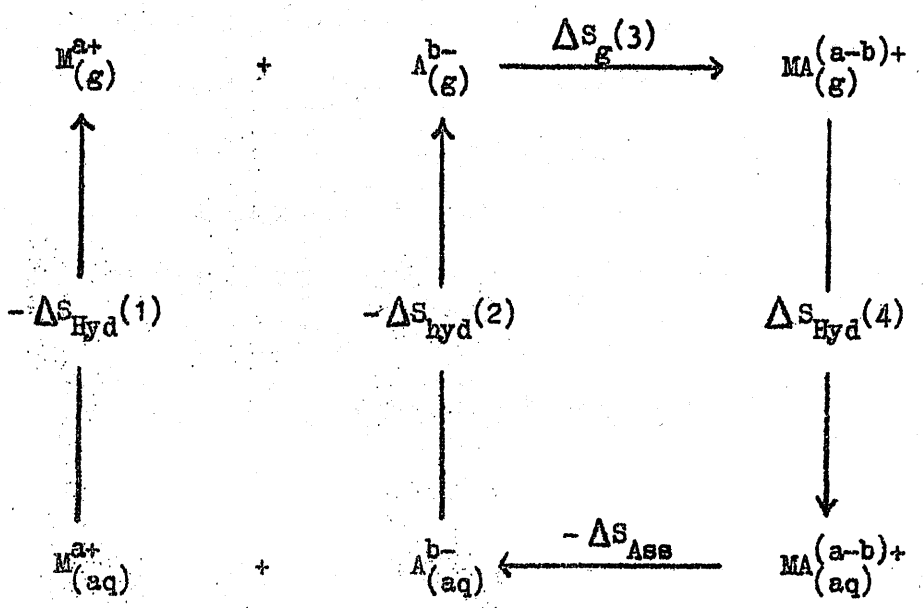
TABLE XII.

Reaction	$-\Delta G$	$-\Delta H$	ΔS.
$Co^{2+} + G^-$	6.89	2.22	15.7
$Co^{2+} + Ox^=$	6.54	-0.59	23.9

Although the stabilities are of the same order, the heats and entropies are quite different for the two complexes, a much more exothermic heat of formation being obtained with the nitrogen containing ligand, glycine.

The entropy change accompanying reactions of the type (1) can be considered to be made up of two parts, a decrease in entropy due to the reduction on the number of solute particles in solution and an increase due to the neutralisation or partial neutralisation, of charge which leads to a decrease in the ordering of solvent molecules. Frank and Evans [58] have suggested that ions in solution orientate the water molecules around them so as to form an effective "iceberg", the process being similar to a partial freezing of the liquid. Thus the removal of ions from the solution, as in the process of complex formation, will lead to a breakdown of this structure and a resulting entropy change favouring complex formation. Since the entropy effect will be related to the ionic charges, a large ΔS will be expected in reactions accompanied by considerable charge neutralisation and a low ΔS in reactions for which there is little charge neutralisation. This explains why the entropy change is greater for ligands containing oxygen rather than nitrogen containing sites.

Writing an entropy cycle [59],



where ΔS_{Hyd} (1) is the entropy change accompanying the hydration of the gas phase cation, ΔS_{Hyd} (2) and $\Delta S_{Hyd}(4)$ are the corresponding values for the anion and the complex and $\Delta S_g(3)$ is the entropy change on association in the gas phase, the observed entropy of association can be written,

$$\Delta S_{Ass} = \Delta S_{Hyd}(4) - \Delta S_{Hyd}(1) - \Delta S_{Hyd}(2) + \Delta S_g(3) \quad \ldots\ldots\ldots(23)$$

$\Delta S_{Hyd}(1)$ and $\Delta S_{Hyd}(2)$ can be obtained from the difference in standard entropy of the ions in the gas (Sg) and the aqueous (S^o) phases. While these are known for a large number of ions [60], they are not known for the glycinate anion. The aqueous phase entropy of the anion was obtained from the crystal entropy, the entropy of hydration, and the entropy of dissociation of glycine. ΔS_{Hyd} for glycine was obtained from solubility measurements at a number of temperatures [61], and $S^o_{A^-}$ was then determined from the dissociation

$$HA \rightleftharpoons H^+ + A^- ,$$

the values being shown in Table X111 .

Table X111.

	S^o_{cryst}	ΔS_{Hyd}	$-\Delta S_{Ass}$	$S^o_{A^-}$
Glycine	26.1 [62]	14.4	-8.8 [46]	+31.7

All entropies in cal./deg.mole.

Where crystal entropies and solubility data are not available, aqueous phase entropies may be calculated from a number of empirical relationships. Powell and Latimer [63] suggested an equation for the entropy of monatomic ions,(based on the standard, $S^{\circ}_{H^+} = 0$).

$$S^{\circ} = 3/2\ R\ln M + 37 - 270z/r_e^2$$

where M is the atomic weight, z the charge and r_e the effective ionic radii of the ions, with corrections for hydration. These corrections were for cations, + 2Å , and for anions + 1Å .

Laidler [64], using the value suggested by Gurney of $S^{\circ}_{H^+} = -5.5$ cal./deg.mole. [51], proposed for monatomic cations the equation,

$$S^{\circ}_{abs.} = 3/2\ R\ln M + 10.2 - 116\ Z^2/r_+$$

which he considered to be theoretically more justified. Equations have been developed by Cobble [65] for the calculation of the entropies of complex oxyanions and simple complexes and he has extended this method to aqueous organic solutes, complexes and chelates. Connick and Powell have also derived an equation for oxyanions [66].

In the gas phase, the entropy change $\Delta S_g(3)$ includes both rotational and translational terms,

$$S_g(3) = S_{trans.}(MA^{(a-b)+}) + S_{rot.}(MA^{(a-b)+}) - S_{trans.}(M^{a+}) - S_{trans.}(A^{b-}) - S_{rot.}(A^{b-}).$$

For monatomic ions in the gas phase only the translational entropy term is involved. $S_{trans.}$ for monatomic ions and diatomic molecules may be obtained from the Sackur - Tetrode equation which, at 25°C, has the form.

$$S_{trans.} = 1.5\ R \ln M + 26.03,$$

where M is the atomic, or molecular weight of the ion.

For symmetrical, non - linear anions, (e.g. SO_4^{2-}), $S_{rot.}(A^{b-})$ may be obtained from the equation,

$$S_{rot.}(A^{b-}) = 2.2868\ (3 \log T + 3 \log I_A - 2 \log \sigma) + 267.52,$$

where I_A is the moment of inertia about the bonds, (S —— O in this case), and σ is the symmetry number [67].

For an ion - pair which can be considered as a linear molecule,

$$S_{trans.} + S_{rot.} = 2.2868\ (7 \log T + 3 \log M + 2 \log I_B - 2 \log \sigma) - 6.661,$$

where I_B is the moment of inertia about its axis [67].

To deal with rigid, non - linear ion - pairs, however, it is necessary to introduce the moments of inertia about the

principal axes [68],

$$S_{trans.} + S_{rot.} = 2.2868\,(8\log T + 3\log M + \log I_A I_B I_C - 2\log \sigma) - 7.697$$

The product $I_A I_B I_C$ of the principal moments of inertia can be calculated by solving the determinant

$$I_A I_B I_C = \begin{vmatrix} +I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & +I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & +I_{zz} \end{vmatrix}$$

where I_{xx} and I_{xy} etc. are the moments and products of inertia with respect to a co-ordinate system having the centre of mass as origin, ie.,

$$I_{xx} = \sum m_i (y_i^2 + z_i^2) \ldots\ldots$$

$$I_{xy} = \sum m_i x_i y_i \ldots\ldots\ldots ,$$

where m_i is the mass of the atom i whose co-ordinates are x_i, y_i, z_i and $\Sigma m_i = M$. X-ray investigation has shown that nickel glycinate is almost planar [69], and this can be assumed for the other glycinate complexes.

It has been shown that the gaseous entropies of cobalt and some other transition metal glycinate complexes are very nearly constant at 57.0 cal.deg^{-1}. mole^{-1}, for both the MA^+ and MA_2 complexes [28], and this value was assumed in the case of the corresponding copper and zinc species. The entropies of the metal ions were those of Staveley and Randall[22].

Substitution of entropy data into equation (23) gave ΔS_{Hyd} (4), the hydration entropy of the complex and the values are listed in Table XIV.

TABLE XIV.

Thermodynamic Properties.

Complex.	S_g complex	$\Delta S_{Assoc.}$	$-\Delta S_{Hyd}(4)$	r_+^{-1}. Å^{-1}
Co G^+	57.0	15.7	36.6	1.35
Cu G^+	57.0	17.8	31.1	1.39
Zu G^+	57.0	14.8	36.0	1.39
Co G_2	56.9	11.3	9.3	1.35
Cu G_2	57.0	10.8	6.4	1.39

all entropies in cal.deg.$^{-1}$mole.$^{-1}$.

The d^9 electronic configuration of copper (II) is capable of additional stabilisation due to tetragonal distortion of the octahedral symmetry as a result of the Jahn - Teller effect. This will result in four short bonds in the xy plane and two long bonds along the z-axis and the effect upon the thermodynamic properties may be two-fold [70]. The increased covalent nature of the shortened metal-ligand bonds in the xy plane will, as has already been discussed, be reflected by a more exothermic enthalpy of formation when the co-ordinating atom in the ligand is nitrogen. It can be seen in Table XI that this is the case with the glycinate complexes. When anionic ligands are involved, the closer contact of the metal and ligand donor atoms in the xy plane will result in a more effective charge neutralisation in the complex and this is reflected in the more positive ΔS_{Hyd} (4) for the copper glycinate complexes (Table XIV), a result which has also been observed for the malonates and succinates [71]. It can also been seen in Table XIV that the entropies of hydration for the MA_2 complexes are much less negative than for the corresponding 1:1 species MA^+, because the former are uncharged.

Since the values of S_g (complex) are similar for all the reactions $\Delta S_{Ass.}$ will therefore be largely determined by differences in hydration. Staveley studied the reactions of ethylene diaminetetraacetate with a number of metal ions and assumed ΔS_{Hyd} (2) and ΔS_{Hyd}(4) to be constant [22]. When, however, ΔS_{Ass} was plotted against $1/r_{m^{2+}}$ three separate curves were obtained. Those for divalent ions with inert gas structures and transition metal ions were linear, but in the case of tervalent ions a curve was obtained. Mancollas has shown, however, that if $\Delta S_{Ass.}$ is plotted against ΔS_{Hyd} (1) a straight line is obtained for all of the complexes [72].

A number of relationships between entropies and the properties of ions have been demonstrated. Latimer found that ΔS_{Hyd} values, based on $S^{o}_{H+} = -2.1$ cal.deg.$^{-1}$ mole^{-1}, were proportional to Z/r', where z was the charge on the ion and r' the effective radius (i.e. $r_- + 0.1$ Å and $r_+ + 0.85$ Å)[73]. Nair and Mancollas have shown that ΔS_{Hyd}(4) varied linearly with $(r_+ + r_-)^{-1}$ for uncharged ion - pairs of 1:1 electrolytes [74]. In the present work neither ΔS_{Hyd}(4) nor $\Delta S_{Ass.}$ varied linearly with $1/r_{M^{2+}}$. George however, has found relationships of the type,

$\Delta S_{Ass} = \Delta S_{Hyd}(2) +$ constant [75]. Different values of the constant are required for different systems and Davies has shown that this value is apparently dependent upon the entropy of hydration of the variable ion [76].

PART II

The Heats of Formation of some Divalent Metal Ion Complexes with EGTA, [di-(2-aminoethoxy)-ethanetetraacetic acid] and EHPG, [diaminoethane N,N'di-(o-hydroxyphenylacetic acid].

PART II.

The Heats of Formation of some Divalent Metal Ion Complexes with EGTA and EHPG.

The complexes formed between the alkaline earth cations and polyaminocarboxylate ligands, (L), form a particularly suitable series for study. If the bonding were purely electrostatic, the order of stability would be expected to follow the inverse order of ionic radii viz.

$$K_{MgL} > K_{CaL} > K_{SrL} > K_{BaL}.$$

Although the last three members invariably conform to this sequence, the association constant for MgL is frequently considerably smaller than that predicted on the basis of simple ionic bonding. Thus the stability constants of the 1:1 complexes of EGTA with Ca^{2+} (logK = 10.93), Sr^{2+}(logK = 8.45), and Ba^{2+}(logK = 8.32) ions [77] are similar to those of the ethylenediaminetetraacetic acid (EDTA) complexes whereas the value for Mg^{2+}(logK = 5.29) is a factor of 10^6 smaller than that for $MgEDTA^{2-}$.

In order to be able to discuss the reason for the observed orders of stability, it is desirable to know the heat and entropy as well as the free energy changes accompanying the association reactions.

From a consideration of free energy data alone, the anomalous behaviour of the magnesium chelates has often been attributed to the difficulty of a multidentate ligand to fold round the small cation sufficiently closely for all its donor atoms to be bound. This would result in fewer bonds being made to the magnesium ion, with the replacement of a smaller number of water molecules from its co-ordination shell. The relatively large and positive entropy changes found for such reactions however, indicate that other factors may be important.

In order to discuss in more detail the important factors involved in the association reactions, precise calorimetric heat changes have been obtained for the association of the EGTA ion with the alkaline earth cations, and with the ions cadmium (II) and zinc (II). Results were obtained for cadmium and zinc in order to compare with the markedly differing results which have been published[78,79] for the complexes Cd EGTA^{2-} and Zn EGTA^{2-}.

The heat data has been combined with known stability constants to give the corresponding entropy changes and the thermodynamic properties for the formation of the alkaline earth complexes are discussed and compared with similar data for other aminocarboxylate complexes.

The heats of formation of the complexes of EHPG with the divalent ions magnesium, calcium, strontium and Barium have been determined in order to provide more thermodynamic data for use in the general discussion of the aminocarboxylate complexes. No values for the heats of protonation of this ligand have been reported and it was necessary to determine these calorimetrically.

Preparation of Reagents:

EGTA: The purity of the EGTA, (Judex Reagent), was estimated by titrating with a standard calcium solution in an ammonia buffer, using eriochrome black T as indicator [80].

EHPG: The solid,(Judex Reagent), was dissolved in a strong base solution and re-precipitated by adding acid to pH 7. This procedure was repeated three times. Percentage elementary analysis figures are shown below, the figures in brackets being the theoretical values based on the formula, $C_{18}H_{20}O_6N_2$.

C	H	O	N
59.54 (59.99)	5.70 (5.60)	27.06 (26.64)	7.70 (7.77)

Potassium Salts of the Ligands:

Standard solutions were prepared by adding sufficient carbonate - free potassium hydroxide to neutralise the four ionisable hydrogens of the acids.

Metal Solutions:

AnalaR metal chlorides were used for all the cations studied with the exception of zinc. Solutions of zinc chloride wereppprepared by the following method. To a weighed amount of zinc oxide was added a slight stoichiometric deficiency of

concentrated AnalaR hydrochloric acid whose chloride content had been checked gravimetrically by precipitation as silver chloride. The solution was shaken until the reaction was complete, then filtered through a low porosity paper. Stock solutions were analysed for zinc by precipitation of the metal as its quinaldinate [80].

Heats of Complex Formation.

The procedure followed for the determination of the heats of complex formation was similar to that described by Care and Staveley for the corresponding EDTA complexes [21]. Relatively concentrated solutions of the potassium salts of EGTA and EHPG, containing a slight excess of potassium hydroxide, were placed in the mixing device. The heats of mixing of identical volumes of these solutions were determined with (1) divalent metal chloride solutions containing sufficient acid to give a suitable final pH, pH_C, the corresponding heat change being Q_C cal., and (11) a solution containing no complexing cation but otherwise identical with solution (1), (heat change, Q_B cal., final pH, pH_B). The ionic strength, in both solutions, was maintained at 0.1 with potassium chloride.

The heats of protonation of EHPG were determined in a similar manner, at an ionic strength of 0.1. The heat of mixing of identical volumes of solutions of the potassium salt of EHPG were determined with, (I) solutions containing varying amounts of hydrochloric acid, (heat change Q'_C cal., final pH, pH'_C), and (II) a blank solution containing only sufficient potassium chloride to maintain the final ionic strength at 0.1, (heat change Q'_B cal., final pH, pH'_B).

Results :

The difference, $(Q_C - Q_B)$, between the heat changes, gave the heat change for the process [21],

$$M^{2+} + H^+_B + OH^-_B + L^{4-}_B + HL^{3-}_B + H_2L^{2-}_B \longrightarrow ML^{2-}_C + L^{4-}_C + HL^{3-}_C + H_2L^{2-}_C + H^+_C + OH^-_C$$

The contrations of all ionic species could be calculated from the measured pH_B and pH_C by using equations for the total metal concentrations,

$$T_m = [M^{2+}] + [ML^{2-}]$$

the total acid concentration,

$$T_L = [ML^{2-}] + [H_2L^{2-}] + [HL^{3-}] + [L^{4-}]$$

electroneutrality,

$$2[M^{2+}] + [KOH] + [H^+] = [OH^-] + 4[L^{4-}] + 3[HL^{3-}] + 2[H_2L^{2-}] + 2[ML^{2-}] + 2T_m ,$$

the complex association constant,

$$K = [ML^{2-}] / [M^{2+}][L^{4-}],$$

and the acid dissociation constants, [71] $K_3 = 1.33 \times 10^{-9}$, and $K_4 = 2.93 \times 10^{-10}$. Values of K at 20°C [77] were corrected to 25°C by using the Van't Hoff equation. The enthalpy change, Q', for the formation of the complex in the reaction

$$M^{2+} + L^{4-} \rightleftharpoons ML^{2-}$$

was then evaluated from $(Q_2 - Q_1)$ by allowing for the heat changes due to the concomitant reactions

$H_2L^{2-} \rightleftharpoons HL^{3-} + H^+$ ($\Delta H_3 = 4.88$ k.cal.mole^{-1}), [71],

$HL^{3-} \rightleftharpoons L^{4-} + H^+$ ($\Delta H_4 = 6.33$ k.cal.mole^{-1}), [71],

and $H^+ + OH^- \rightleftharpoons H_2O$

The results for EGTA are given in Tables XV to XX.

Table XV.

Heat of Formation of $MgEGTA^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	$-Q_c$ (cal.)	$-Q'$ (cal.)
1	300	-24.3	0.110	-2.66	-3.60
2	300	-27.1	0.105	-2.84	-3.77
3	300	-20.5	0.146	-2.99	-3.79
4	300	-21.5	0.129	-2.77	-3.85

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_a.10^3$	$ML^{2-}.10^3$	ΔH (k.cal.mole^{-1}.)
1	2.500	2.690	2.284	+5.25
2	2.500	2.678	2.283	+5.51
3	2.500	2.673	2.302	+5.49
4	2.500	2.682	2.246	+5.71

Mean $\Delta H = +5.49 \pm 0.12$ k.cal.mole^{-1}.

Table XVI.

Heat of Formation of $CaEGTA^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	$-Q_c$ (cal.)	$-Q^o$ (cal.)
1	300	67.0	0.108	+7.22	+5.86
2	300	66.7	0.106	+7.07	+5.96
3	300	62.3	0.115	+7.18	+6.07
4	300	64.2	0.110	+7.06	+5.94

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_a.10^3$	$ML^{2-}.10^3$	ΔH (k.cal.mole^{-1}.)
1	2.500	2.676	2.500	-7.82
2	2.500	2.673	2.500	-7.94
3	2.500	2.674	2.500	-8.08
4	2.500	2.673	2.500	-7.92

Mean $\Delta H = -7.94 \pm 0.07$ k.cal.mole^{-1}.

Table XVII.

Heat of Formation of $SrEGTA^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	$-Q_c$ (cal.)	$-Q'$ (cal.)
1	300	45.5	0.120	+5.47	+4.24
2	300	47.8	0.117	+5.60	+4.48
3	300	40.9	0.130	+5.33	+4.08
4	300	43.5	0.127	+5.51	+4.33
5	300	49.2	0.112	+5.52	+4.38

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_s.10^3$	$ML^{2-}.10^3$	ΔH (k.cal.mole^{-1}.)
1	2.500	2.673	2.500	-5.65
2	2.500	2.675	2.500	-5.98
3	2.500	2.674	2.500	-5.44
4	2.500	2.673	2.500	-5.77
5	2.500	2.672	2.500	-5.84

Mean $\Delta H = -5.74 \pm 0.15$ k.cal.mole^{-1}.

Table XVIII.

Heat of Formation of $BaEGTA^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	$-Q_c$ (cal.)	$-Q'$ (cal.)
1	300	84.2	0.095	+8.01	+6.65
2	300	69.2	0.119	+8.21	+7.01
3	300	65.4	0.120	+7.87	+6.54
4	300	65.5	0.118	+7.72	+6.54
5	300	72.0	0.111	+7.96	+6.79
6	300	76.7	0.105	+8.06	+6.91

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_a.10^3$	$ML^{2-}.10^3$	ΔH (k.cal.mole^{-1}.)
1	2.500	2.674	2.500	-8.87
2	2.500	2.673	2.500	-9.34
3	2.500	2.675	2.500	-8.72
4	2.500	2.674	2.500	-8.72
5	2.500	2.673	2.500	-9.05
6	2.500	2.671	2.500	-9.21

Mean $\Delta H = -8.99 \pm 0.22$ k.cal.mole^{-1}.

Table XIX.

Heat of Formation of $CdEGTA^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	$-Q_c$ (cal.)	$-Q'$ (cal.)
1	300	67.9	0.155	+10.52	+11.42
2	300	49.1	0.204	+10.03	+10.90
3	300	43.7	0.236	+10.29	+11.12
4	300	44.0	0.232	+10.24	+11.11
5	300	57.6	0.180	+10.39	+11.27

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_a.10^3$	$ML^{2-}.10^3$	ΔH (k.cal.mole^{-1}.)
1	2.500	2.667	2.500	-15.23
2	2.500	2.672	2.500	-14.53
3	2.500	2.670	2.500	-14.83
4	2.500	2.674	2.500	-14.81
5	2.500	2.672	2.500	-15.03

Mean $\Delta H = -14.89 \pm 0.20$ k.cal.mole^{-1}.

Table XX.

Heat of Formation of $ZnEGTA^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	$-Q_c$ (cal.)	$-Q'$ (cal.)
1	300	16.7	0.159	+2.65	+3.82
2	300	15.3	0.165	+2.52	+3.68
3	300	15.6	0.160	+2.50	+3.66
4	300	13.0	0.206	+2.68	+3.84
5	300	14.6	0.182	+2.66	+3.82

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_s.10^3$	$ML^{2-}.10^3$	ΔH (k.cal.mole^{-1}.)
1	2.500	2.671	2.500	-5.09
2	2.500	2.675	2.500	-4.91
3	2.500	2.675	2.500	-4.88
4	2.500	2.673	2.500	-5.12
5	2.500	2.674	2.500	-5.09

Mean $\Delta H = -5.02 \pm 0.10$ k.cal.mole^{-1}.

To calculate the heats of protonation of EHPG, the concentration of acid species were determined from the expression for the total acid concentration

$$T_L = [H_2L^{2-}] + [HL^{3-}] + [L^{4-}],$$

the dissociation constants of EHPG [81], k_3, = 2.630×10^{-11} and k_4 = 1.201×10^{-12}, and the measured pN values, pH'_C and pH'_B. The changes in acid species concentrations were then equated to the differences in the heat changes $(Q'_C - Q'_B)$ cal. after correcting for the heat changes due to the formation of water, Q_{H_2O} cal. The results are shown in Table XXI.

With a knowledge of ΔH_3 and ΔH_4 for the protonation reactions, and using the association constants [81] log $K(MgL^{2-})$ = 8.0 and log $K(CaL^{2-})$ = 7.2, the heats of formation of the magnesium and calcium complexes were calculated. The association constants for the formation of the strontium and barium monocomplexes with EHPG have not been determined and in order to calculate the heats of formation it was assumed that association constants were of the same order as that for calcium. It was felt that this assumption was justified since other polyaminocarboxylate complexes have similar association constants for these metal ions [77,78]. The results are given in Tables XXII to XXV.

Table XXI.

Heats of Protonation of EHPG at 25°C (I = 0.1).

Molar concentrations of ionic species

	$[Y^{4-}]$	$[HY^{3-}]$	$[H_2Y^{2-}]$	$[OH^-]$
Blank.	$6.1613.10^{-4}$	$4.5290.10^{-3}$	$1.5206.10^{-3}$	$1.142.10^{-3}$
Run 1.	$1.6157.10^{-5}$	$1.3673.10^{-3}$	$5.2837.10^{-3}$	$9.918.10^{-5}$
Run 2.	$4.7733.10^{-5}$	$2.1953.10^{-3}$	$4.4607.10^{-3}$	$1.855.10^{-4}$

	Heat Evolved (cals.)	$-Q_{H_2O}$ (cals.)
Blank.	-3.2376	
Run 1.	+5.6888	+4.2530
Run 2.	+4.4079	+3.9009

Changes in amounts of species from Blank to Run

	$-\Delta[Y^{4-}]$ (moles)	$\Delta[H_2Y^{2-}]$ (moles)	$-Q_{corr}$ (cals.)
Run 1.	$1.7999.10^{-4}$	$1.1289.10^{-3}$	+4.6734
Run 2.	$1.7052.10^{-4}$	$0.6820.10^{-3}$	+3.7446

ΔH_3 $(H_2Y^{2-} \longrightarrow H^+ + HY^{3-})$ = +3.64 k.cal.mole^{-1}.

ΔH_4 $(HY^{3-} \longrightarrow H^+ + Y^{4-})$ = +3.12 k.cal.mole^{-1}.

Table XX11.

Heat of Formation of $MgEHPG^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. ($cal.unit^{-1}$)	$-Q'_c$ (cal.)	$-Q_{corr}$ (cal.)
1	300	-10.7	0.1136	-1.216	-0.557
2	300	-13.4	0.1090	-1.460	-1.043

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_a.10^3$	$ML^{2-}.10^3$	ΔH ($k.cal.mole^{-1}$)
1	1.167	1.333	1.167	+1.59
2	1.333	1.667	1.333	+2.61

Mean $\Delta H = +2.10 \pm 0.51$ $k.cal.mole^{-1}$.

Table XX111.

Heat of Formation of $CaEHPG^{2-}$

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal.unit^{-1})	$-Q'_c$ (cal.)	$-Q_{corr}$ (cal.)
1	300	-12.4	0.1221	-1.514	+1.102
2	300	-13.1	0.1203	-1.576	+1.245

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_a.10^3$	$ML^{2-}.10^3$	ΔH (k.cal.mole^{-1})
1	1.167	1.333	1.167	-3.15
2	1.333	1.667	1.333	-3.11

Mean $\Delta H = -3.13 \pm 0.02$ k.cal.mole^{-1}.

Table XX1V.

Heat of Formation of $SrEHPG^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. ($cal.unit^{-1}$)	$-Q'_c$ (cal.)	$-Q_{corr}$ (cal.)
1	300	-16.1	0.1153	-1.857	+0.708
2	300	-15.9	0.1196	-1.902	+0.663
3	300	-20.5	0.0821	-1.684	+0.792

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_a.10^3$	$ML^{2-}.10^3$	ΔH ($k.cal.mole^{-1}$)
1	1.167	1.333	1.167	-2.02
2	1.167	1.333	1.167	-1.89
3	1.333	1.667	1.333	-1.98

Mean $\Delta H = -1.96 \pm 0.06$ $k.cal.mole^{-1}$.

Table XXV.

Heat of Formation of $BaEHPG^{2-}$.

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E ($cal.unit^{-1}$)	$-Q'_c$ (cal.)	$-Q_{corr}$ (cal.)
1	300	-16.9	0.1189	-2.010	+0.657
2	300	-18.5	0.1206	-2.232	+0.612

Molar concentrations of ionic species

Run	$T_m.10^3$	$T_B.10^3$	$ML^{2-}.10^3$	ΔH ($k.cal.mole^{-1}$)
1	1.167	1.333	1.167	-1.88
2	1.333	1.667	1.333	-1.53

Mean $\Delta H = -1.71 \pm 0.18$ $k.cal.mole^{-1}$.

Discussion :

The thermodynamic properties for the EGTA complexes are given in Table XXVI . Since this work was done, there have been published calorimetric results at 20°C. obtained by Anderegg [79] for the divalent magnesium, calcium, zinc and cadmium ions. The values are given in parentheses in Table XXVI and the agreement with the present work is seen to be satisfactory.

TABLE XXVI.

Thermodynamic Properties for the Formation of $MEGTA^{2-}$ Complexes.

Metal Ion	$-\Delta G$ ($k.cal.mole^{-1}$)	ΔH ($k.cal.mole^{-1}$)	ΔS ($cal.deg^{-1}.mole^{-1}$).
Mg^{2+}	7.20	+5.49 (5.18)	42.6
Ca^{2+}	14.86	-7.94 (-8.38)	23.2
Sr^{2+}	11.50	-5.74	19.3
Ba^{2+}	11.32	-8.99	7.8
Zn^{2+}	17.55	-5.02 (-4.28)	42.1
Cd^{2+}	12.55	-14.89 (-14.8)	25.7

The entropy of association can be written,

$$\Delta S = S^{\circ}(ML^{2-}) - S^{\circ}(M^{2+}) - S^{\circ}(L^{4-}) \quad \ldots\ldots\ldots\ldots\ldots \quad (24)$$

where S° is the standard aqueous entropy of the species enclosed in brackets. For the formation of 1:1 complexes between an anion and a series of cations, equation (24) may be conveniently re-arranged to give [80]

$$\Delta S + S^{\circ}(M^{2+}) = \underbrace{\left[S_g(ML^{2-}) - S_g(L^{4-})\right]}_{I} + \underbrace{\left[S_{hyd}(ML^{2-}) - S_{hyd}(L^{4-})\right]}_{II} \quad \ldots(25)$$

in which S_g and S_{hyd} are the gas phase and hydration entropies respectively. Values of $\left[\Delta S + S^{\circ}(M^{2+})\right]$ are given in the table XXVII for EGTA at 25°C. and other aminocarboxylate ligands at 20°C. for which alkaline earth data are available. The difference in temperature will not affect the following arguments.

TABLE XXVII

Values of $\Delta S + S^{\circ}(M^{2+})$ for 1:1 Metal Aminocarboxylate Compl.

Metal Ion	EDTA[82]	CDTA[82]	EGTA	BATA[83]
Mg^{2+}	22.8	34.9	14.4	21.8
Ca^{2+}	13.4	34.3	10.0	9.2
Sr^{2+}	16.2	36.3	9.9	-
Ba^{2+}	21.7	43.9	10.8	-

The right hand side of equation (25) contains terms in ML^{2-} and L^{4-}. Term I reflects the change in configurational and librational entropy of the ligand molecule when it enters into complex formation. The increase in translational entropy will be small, and, since the ligand loses freedom, this term will be negative. The negative hydration entropy of the ion L^{4-} will be greater than that of the lower charged ML^{2-} resulting in a positive term II in equation (25). The positive values of $\left[\Delta S + S^{o}(M^{2+})\right]$ in Table XXVII indicate that term II represents the overriding factor for these metal ions.

Following Kroll and Gordon [84], it is convenient to divide the polyaminoacetate acid chelates into three groups.

(I) those with the EDTA skeleton, including the carbocyclic cyclohexanediaminetetraacetic acid, CDTA,

(II) those with an additional potential co-ordinating atom, X, in the central chain, having the general formula

$(^{-}OOCCH_2)_2 N (CH_2)_2 X (CH_2)_2 N (CH_2COO^{-})_2$

where X = O, (EATA); = NCH_2COO^{-}, (DTPA), etc.

(III) those with two potential co-ordinating centres in the central chain,

$(^{-}OOCCH_2)_2\ N\ (CH_2)_2\ X\ (CH_2)_2\ X\ (CH_2)_2\ N\ (CH_2COO^{-})_2$.

where X = O, (EGTA) ; = NCH_3 (BDAM).

The trends in the available ΔG, ΔH and ΔS for the alkaline earth cations are illustrated in Figure 11. Unfortunately ΔH and ΔS have not been determined for any strontium or barium complexes of groups (ii) ligands and it is possible to include only the calcium and magnesium values. For DTPA, the ΔG values are plotted for comparison [77]. The figure illustrates a number of characteristic patterns of behaviour. In group (i), the greater stability of CDTA complexes as compared with those of EDTA is primarily the result of a much more favourable entropy term $\left[\Delta S + S^{o}(M^{2+})\right]$ for the former which outweighs the unfavourable ΔH difference. The explanation lies in the fact that in CDTA, the two N atoms are restricted in their movement by the carbocyclic chain and so term I in equation (25) will be more positive than for EDTA. In addition it has been suggested that as the carboxyl groups are held more rigidly in CDTA than in EDTA, the resulting localisation of charge will lead to a more effective orientation of water molecules making $-\Delta S_{Hyd}\ (CDTA^{4-}) > -\Delta S_{Hyd}\ (EDTA^{4-})$ and term II equation (25) more positive for CDTA[82].

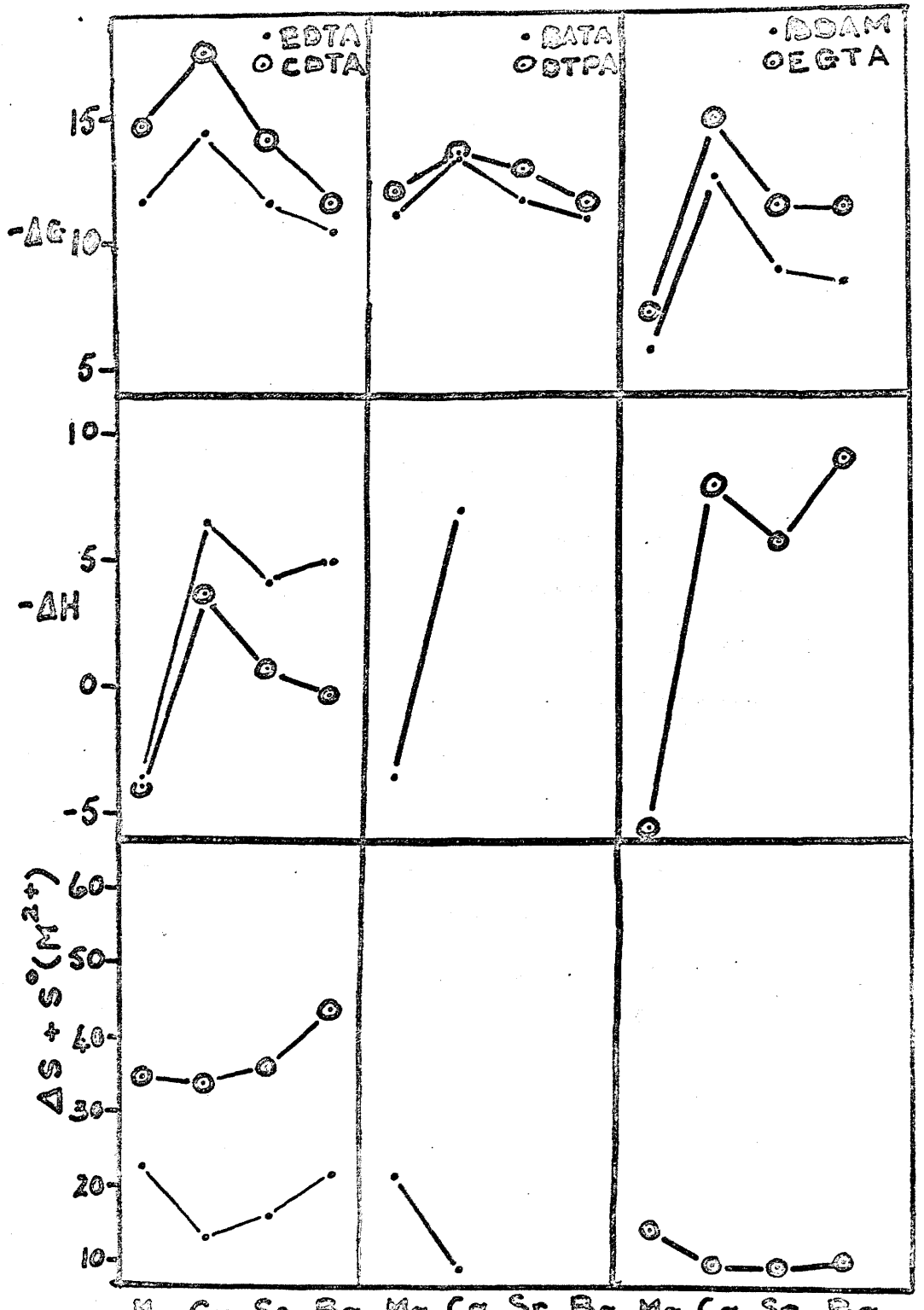

• EDTA
○ CDTA
• DATA
○ DTPA
• DDAM
○ EGTA
-ΔG
15
10
5
-ΔH
10
5
0
-5
ΔS + S°(M2+)
60
50
40
30
20
10
Mg Ca Sr Ba Mg Ca Sr Ba Mg Ca Sr Ba

Fig 11.

The increased endothermicity accompanying the formation of CDTA complexes is a consequence of the steric hindrance imposed by the cyclohexyl ring [82]. The value of $\Delta G\ (MgL^{2-}) - \Delta G(CaL^{2-})$ is about the same for both EDTA and CDTA but the heat and entropy trends are quite different. In going from calcium to magnesium, there is an appreciable increase in $\left[\Delta S + S^{\circ}\ (M^{2+})\right]$ for EDTA compared with that for CDTA indicating a smaller positive contribution in term II (equation 25) for CDTA. It is possible that $MgCDTA^{2-}$ is more hydrated than $MgEDTA^{2-}$ since there is a considerable strain involved in completing the co-ordination of the rigid $CDTA^{4-}$ anion to the small magnesium ion. Some support for this suggestion is provided by the rather large drops in $-\Delta H$, in the figure, for the formation of $MgEDTA^{2-}$.

There are very few thermodynamic properties available for the group (iii) ligands although it is seen in the figure that the general trends are similar to those in group (i) with a rather smaller difference in ΔG between the calcium and strontium chelates. Group (iii) has two members for which stability constants have been measured and the results of the present work provide detailed thermodynamic date for one of them, EGTA.

The complexes are characterised by a particularly large increase in stability in going from magnesium to calcium. $\left[\Delta S + S^{o}(M^{2+})\right]$ values for EGTA differ very little, indicating a similar structure for all the complexes in the series. The results of N.M.R. studies [85] lend support to this suggestion and it appears that both ether oxygen atoms in the central chains are involved in the bonding to the metal ion. The drop in stability at magnesium is clearly the result of the more endothermal ΔH reflecting the increased potential energy involved in the interaction between the small Mg^{2+} ion and the negatively charged $EGTA^{4-}$ ion. Considerable strain is imposed in bringing the co-ordinating centres sufficiently close for stable electrostatic bonds to be formed.

The smaller $\left[\Delta S + S^{o}(M^{2+})\right]$ values for EGTA as compared with EDTA complexes may be caused by two factors.

(1) The greater loss of configurational entropy of the larger EGTA molecule when it interacts with the metal ions.

(11) The two carboxylate groups which remain free in the EGTA complexes and which will retain some solvent ordering properties whilst not being able, through negative charge repulsion, to make full use of their mobility.

In order to be able to discuss the formation of aminocarboxylate complexes in solution more fully, many more precise thermodynamic data are required. To this end the heats of formation of the alkaline earth complexes with EHPG were determined. The thermodynamic data are shown in Table XXVIII. The ΔG values for the formation of the strontium and barium species have not yet been determined.

TABLE XXVIII

THERMODYNAMIC PROPERTIES FOR THE FORMATION OF M EHPG^{2-} COMPLEXES

METAL ION	$-\Delta G$ (k.cal.mole^{-1})	$-\Delta H$ (k.cal.mole^{-1})	ΔS (cal.deg^{-1}.mole^{-1})
Mg^{2+}	10.87	-2.10	43.5
Ca^{2+}	9.78	+3.13	22.3
Sr^{2+}	-	+1.96	-
Ba^{2+}	-	+1.71	-

The acid dissociation constants for EHPG [81], $k_3 = 2.630 \times 10^{-11}$ and $k_4 = 1.201 \times 10^{-12}$, are considerably smaller than those for EGTA. The heat corrections for the formation of water are, therefore, considerably larger than those for EGTA and the resulting heats of protonation, and

heats of complex formation are considerably more inaccurate. It can be seen however, that the trends in the ΔH values for the HEPG complexes are similar to those of EGTA.

The high stabilities of aminopolycarboxylate and polyamine complexes is usually attributed to what has been termed a "chelate effect". In the formation of a complex with a multidentate ligand, less translational entropy will be lost than when the metal forms a complex with an equivalent number of unidentate ligands. The magnitude of this chelate effect can be seen by comparing the data for the nickel complexes of ethylenediamine, (en), and ammonia [86, 87],

$Ni^{2+}_{aq} + 6\ NH_3 \rightleftharpoons Ni(NH_3)^{2+}_6 + xH_2O,\ -\Delta G = 0.01$ k.cal.mole^{-1},

and $Ni^{2+}_{aq} + 3\ en \rightleftharpoons Ni(en)^{2+}_3 + xH_2O,\ -\Delta G = 5.90$ k.cal.mole^{-1}.

Both ligands co-ordinate with metals through their N atoms but the complex with en. is considerably more stable than that with the monodentate ligand.

It has been shown for many systems, that for a given number of donor atoms in the complex, the ΔS values increase as the number of chelate rings increases. The chelate effect is, therefore, largely an entropy effect which can be ascribed to the increase in the number of free solute particles

accompanying complex formation with a consequent increase in ΔS_g in the entropy cycle (Part I). While this is so, the enthalpy terms cannot be ignored. The formation of nickel ammonia complexes takes place with a more endothermic heat change than for the corresponding ethylenediamines, and the differences in the experimental functions, $\Delta H\left[Ni(en)_x\right] - \Delta H\left[Ni(NH_3)_{2x}\right]$ are - 1.05 , - 1.90 and - 2.90 k.cal.mole^{-1}. for x = 1, 2 and 3 respectively. These values are quite close to the differences in ligand - field stabilisation energy in the two types of complexes , - 0.90, - 1.85 and - 2.75 k.cal.mole^{-1}. respectively [88].

The favourable enthalpy changes accompanying chelate formation for these complexes, has been attributed by Williams to a "built-in" effect [89]. Once one of the N atoms of the en. molecule is co-ordinated to the metal ion, the other N atom is held in place by the rest of the molecule. In forming the complex with the monodentate ligand, on the other hand, mutual repulsions of the polar groups must be overcome in bringing up the second ligand molecule so that this stage of the reaction will be more endothermic. When the intervening methylene chain becomes long, however, a multidentate ligand may behave as separate unidentate centres since the freedom of

unco-ordinated donor atoms may be relatively unrestricted. In this case the stabilities of complexes may resemble more closely those of equivalent unidentate ligands.

PART III

The Heat of Hydrolysis of the Thallic Ion Tl(III)

PART III.

The Heat of Hydrolysis of Thallic Ion, Tl(III).

Introduction:

When the first Tl(III) salt was prepared, about one hundred years ago [90], it was observed that it was stable only in solutions of high acidity. On decreasing the hydrogen ion concentration, the salt was decomposed by water with the formation of an insoluble product. The Tl(III) ion is, therefore, an acid of considerable strength and it reacts with water producing hydrogen ions. Abegg and Spencer [91], when investigating equilibria in solutions containing Tl(III), Tl(I) ions and different anions, determined the stability of Tl_2O_3 in nitric acid solutions. From the constancy of the ratio $[Tl^{3+}] / [H^+]^3$, they concluded that the hydrolysis proceeded according to the reaction.

$$Tl^{3+} + 3H_2O \longrightarrow Tl(OH)_3\ (S) + 3\ H^+.$$

It was found later by Hüttig and Mytyzek [92], and by Mulligan and Weiser [93], that the X-radiograms of the wet precipitate and anhydrous Tl_2O_3 were identical, so the above reaction must be written $2Tl^{3+} + 3H_2O \longrightarrow Tl_2O_3(S) + 6\ H^+$.

Several investigators [91,94] have observed that the formal redox potential Tl(I) - Tl(III) decreases with decreasing $[H^+]$ and this was ascribed to the hydrolysis of the Tl(III) ion. Although all investigators working with the Tl(III) ion were well aware of its strong hydrolysis it was not until just over ten years ago that the soluble species formed when Tl(III) reacted with water, and the equilibrium constants of the hydrolysis processes, were determined [95].

The aim of the present work was to investigate these processes further by determining the enthalpies of the hydrolysis reactions.

$$Tl(III) + H_2O \rightleftharpoons TlOH^{2+} + H^+ \quad \ldots\ldots\ldots\ldots (1)$$

and

$$TlOH^{2+} + H_2O \rightleftharpoons Tl(OH)_2^+ + H^+ \quad \ldots\ldots\ldots\ldots (2)$$

Preparation of Reagents:

Thallous Perchlorate.

AnalaR thallous nitrate was dissolved in an excess of hot concentrated AnalaR perchloric acid. The precipitated thallous perchlorate was washed, recrystallised three times from distilled water and dried at 120°C. The purity of the solid was determined by titrating with standard potassium iodate in concentrated hydrochloric acid [80].

Perchloric Acid.

AnalaR perchloric acid was used without further purification.

Thallic Perchlorate.

Solutions were prepared by anodic oxidation of thallous perchlorate in 2 M perchloric acid [95], and estimated by adding an excess of potassium iodide and titrating the liberated iodine with standard sodium thiosulphate using a starch indicator. The absence of any Tl(I) ion could be checked by adding potassium iodate to the solutions, as in the estimation of thallous perchlorate, and observing no iodine colour.

Sodium Perchlorate.

AnalaR sodium carbonate was recrystallised twice from boiling distilled water. The solid was then added to perchloric acid until the solution was neutral (B.D.H Indicator). The sodium perchlorate was precipitated by adding an excess of perchloric acid to the solution. Solutions of the salt were analysed by determining the free acid concentration with standard sodium hydroxide and subtracting this from the total acid concentration after passing the solution through an Amberlite I.R. 120 ion - exchange column in the hydrogen form.

Experimental.

The calorimeter has already been described in Part I. Solutions of thallic perchlorate in 1M perchloric acid were placed in the mixing device and the ionic strength was maintained at a value of 3 M with sodium perchlorate. These solutions were mixed into perchloric acid solutions of the same ionic strength in the Dewar vessels. For each run, the heat of dilution of the mixing device solution was determined by replacing the thallic salt with sodium chloride of the same ionic strength, all other concentrations being the same as in the corresponding complexing experiment.

Method of Calculation:

The concentration of species in solution were calculated from the equations for the association constants [95], ca

$$k_1 = \left[TlOH^{2+}\right]\left[H^+\right] / \left[Tl^{3+}\right] = 7.25 \times 10^{-2},$$

$$k_2 = \left[Tl(OH)_2^+\right]\left[H^+\right] / \left[TlOH^{2+}\right] = 3.25 \times 10^{-2},$$

and the expression for the total metal ion concentration,

$$T_m = \left[Tl^{3+}\right] + \left[TlOH^{2+}\right] + \left[Tl(OH)_2^+\right].$$

Results and Discussion.

Some results of the calorimetric experiments are summarised in Table XXIX.

TABLE XXIX.

Molar Concentrations of Ionic Species.

RUN 4.

	Before Mixing	After Mixing	Concentration Change
$TlOH^{2+}$	1.697×10^{-3}	2.988×10^{-3}	1.291×10^{-3}
$Tl(OH)_2^+$	5.515×10^{-5}	1.823×10^{-4}	1.271×10^{-4}

Experimental Heat Change = 0.0 cals.

RUN 5.

$TlOH^{2+}$	1.697×10^{-3}	3.566×10^{-3}	1.869×10^{-3}
$Tl(OH)_2^+$	5.515×10^{-5}	2.675×10^{-4}	2.123×10^{-4}

Experimental Heat Change = 0.0 cals.

It is seen that the heat changes for the above runs were negligibly small, as they were for all experiments even though the change in $[TlOH^{2+}]$ was greater than 1×10^{-3} moles. l^{-1}. Since the Tl(III) ion forms very stable complexes with chloride ion, ($\log K\ (TlCl^{2+}) = 6.25$, $\log K\ (TlCl_6^{3-}) = 1.30$)[96], it was felt that traces of chloride present as impurity may have complexed with the Tl(III) and thus prevented its hydrolysis. Although further precautions were taken to remove Cl^- ion from the sodium perchlorate and perchloric acid solutions, the resulting experimental heat changes were still negligibly small.

It would be desirable to measure the heats of hydrolysis in solutions which have undergone even more stringent purification.

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